

Review

Application of Mesoporous/Hierarchical Zeolites as Catalysts for the Conversion of Nitrogen Pollutants: A Review

Małgorzata Rutkowska *  and Lucjan Chmielarz 

Faculty of Chemistry, Jagiellonian University, Gronostajowa 2, 30-387 Krakow, Poland; lucjan.chmielarz@uj.edu.pl

* Correspondence: malgorzata.rutkowska@uj.edu.pl; Tel.: +48-12-686-24-29

Abstract: Mesoporous/hierarchical zeolites (HZs) are a relatively new group of materials, and interest in their application in catalysis is continuously growing. This paper presents recent achievements in the application of mesoporous zeolites in catalytic reactions of nitrogen pollutant conversion. The analysis presented includes processes such as selective catalytic reduction of NO_x with ammonia (NH₃-SCR, DeNO_x), selective catalytic oxidation of ammonia (NH₃-SCO, AMO_x), and catalytic decomposition of N₂O. Different zeolite topologies and methods of their modification focused on mesoporosity generation (e.g., desilication, dealumination, steaming, self-assembly techniques, and application of hard and soft templates) are reviewed and compared with respect to catalytic processes. Special attention is paid to the role of porous structure and acidity, as well as the form of deposited transition metals, in the catalytic activation of modified zeolites in the elimination of nitrogen pollutants from flue gases.

Keywords: mesoporous zeolites; hierarchical zeolites; nitrogen pollutants; NH₃-SCR; NH₃-SCO; N₂O decomposition



Citation: Rutkowska, M.; Chmielarz, L. Application of Mesoporous/Hierarchical Zeolites as Catalysts for the Conversion of Nitrogen Pollutants: A Review. *Catalysts* **2024**, *14*, 290. <https://doi.org/10.3390/catal14050290>

Academic Editor: Avelina García-García

Received: 5 April 2024

Revised: 15 April 2024

Accepted: 23 April 2024

Published: 25 April 2024



Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Mesoporous/Hierarchical Zeolites in Catalysis

Zeolites are materials that have been successfully used in catalysis since the 1950s, especially in petroleum refining processes such as fluid catalytic cracking (FCC), alkylation, methanol-to-hydrocarbons (MTH) conversion, isomerisation, or hydroconversion. Numerous advantages of zeolites, such as well-defined pore sizes and excellent shape selectivity, large number of structure types, tunable/strong acidity, high crystallinity, high thermal stability, ion exchange properties, or various possibilities of their modification, cannot be effectively used in catalysis because of the hindered access to the internal pore system. The microporosity of zeolites (the presence of pores with diameter < 2 nm, practically in the range of 0.3–0.75 nm) causes diffusion limitations due to the similar or larger dimensions of the catalysed molecules than the pore sizes. In this case, the overall reaction rate is limited by the diffusion rate, and the reaction may proceed mainly on the outer surface of the catalyst grains. Another problem related to diffusion limitations is the blocking of pores due to the formation of carbon deposits, resulting in catalyst deactivation [1–3].

The applicability of zeolites in catalysis can be enhanced by the generation of a secondary pore system within the zeolite crystals. Zeolites with bimodal porosity, called mesoporous zeolites (sometimes also hierarchical zeolites HZs, hierarchically structured zeolites, or extra-large pore zeolites), combine an additional system of larger pores (mesopores or macropores) with the conventional system of micropores. The idea of materials that combine the properties of zeolites with systems with larger pores can also be realised by intercrystalline mesoporosity (reduction in the size of zeolite grains, nanozeolites) or by the preparation of zeolite composites (micro-mesoporous zeolitic composites, MZCs) [3]. Methods of modification of zeolites toward the generation of a secondary pore system have been developed and investigated for the past 20 years. Numerous pathways for the synthesis of bimodal porosity have been described in the literature. Generally, these methods can

be classified into two groups: top-down and bottom-up. In the former group (top-down, also called destructive) are methods that rely on the post-synthesis modification of zeolites (synthesised by conventional methods or commercially available). The most popular top-down methods include desilication, dealumination, recrystallisation, and modification of 2D (layered) zeolites. The second group (bottom-up, constructive) includes methods based on the creation of a secondary pore system during the synthesis of zeolites [2]. Examples include template methods (both soft and hard) and template-free methods (by controlling the synthesis conditions), the synthesis of zeolite nanoparticles, zeolites with new grain morphologies, such as hollow spheres, or even the use of 3D printing technology. A brief description of these methods (an explanation of what the modification is, its conditions, and the most important comments on its advantages and disadvantages) is summarised in Table 1. A comprehensive and broad presentation of mesoporous zeolite synthesis methods can be found in the following review articles [1–9].

The first application of modified zeolites in catalysis was connected with ultrastabilisation (by steaming or acid treatment) of zeolite Y to prepare USY. Zeolite Y has been known as an active catalyst for fluid catalytic cracking (FCC) since the early 1960s [10]; however, its potential is still not used effectively. Partial extraction of framework Al^{3+} cations by steam or acid hydrolysis of the Al–O–Si bond with the formation of mesopores significantly increased the hydrothermal stability of USY zeolite. This modification enhanced the attractiveness of zeolite Y in FCC and hydrocracking processes; however, studies on its modification by different methods (e.g., soft- and hard-templating, desilication, and dealumination) are still ongoing [11]. As an example, commercial FCC mesostructured zeolite Y, prepared by surfactant-templated post-synthetic modification (Rive Technology) on an industrial scale in 2013, was successfully implemented [12,13].

The rapid development of hierarchical zeolite synthesis methods observed during recent decades is correlated with the wide range of their applications in catalysis. The main area of the potential utilization of HZs is correlated with acid functionality in the petrochemical industry. Mesoporous zeolites presented superior catalytic performance (in comparison to conventional zeolites) in catalytic cracking (e.g., cumene, n-hexane, n-dodecane, vacuum gas oil, and waste cooking oil), alkylation (e.g., benzene, toluene, phenol, naphthalene, ethyl benzene, and isobutane), methanol-to-hydrocarbon conversion (e.g., methanol to gasoline, methanol to olefins), aromatization (e.g., ethane), biomass conversion (e.g., lignocellulosic), and isomerisation (e.g., m-xylene, n-pentane, n-butene, and n-hexadecane) [3,14]. Moreover, zeolites were found to be effective bifunctional catalysts, e.g., in the reactions requiring acidic and metallic functionalities, such as Pt and Co, and in hydroconversion processes, e.g., hydrocracking, hydroisomerisation, hydrodesulphurisation, and hydrodealkylation. Mesoporous zeolites, which ensure a good distribution of metals, were found to be more active or/and selective compared to their classical counterparts [14,15].

Another group of catalytic reactions, in which the utilisation of hierarchical zeolites is gaining a lot of interest, is related to environmental issues [16]. As an example, the synthesis of green alternative fuels, such as dimethyl ether (DME), can be mentioned. DME, which can be used as a biofuel for diesel engines, can be obtained by methanol dehydration over catalysts containing acid sites. However, strong acid sites, together with the microporous pore architecture of zeolites, favour the formation of byproducts and fast catalyst deactivation by coke deposits. The mesoporous ZSM-5 zeolites obtained by the mesotemplate-free method (bottom-up method) [17] or by desilication (top-down method) [18] presented improved selectivity of the reaction to DME. Another example of the application of hierarchical zeolites in environmental catalysis is volatile organic compound (VOC) incineration. The emission of VOCs into the atmosphere, which is very dangerous both for human health and the environment (impact on the destruction of the ozone layer, global warming, and formation of photochemical smog), can be reduced by their catalytic oxidation. Wang et al. [19,20] investigated the activity of different Pt-zeolites (ZSM-5, Beta, USY, and S-1) modified by desilication with a TPAOH solution in low-temperature oxidation of benzene, n-hexane, ethyl acetate, and acetonitrile. The studies

performed showed the correlation between the hierarchical porous structure, form, and aggregation of Pt nanoparticles and their catalytic activity in the oxidation of VOCs. The porous structure of zeolites modified by the generation of mesopores favours the deposition of small and well-dispersed Pt nanoparticles, which promote the catalytic oxidation of aromatics and alkanes.

Beyond the variety of catalytic reactions involving organic molecules, hierarchical zeolites have also found application as catalysts for the conversion of inorganic molecules [21]. Modification of the porous structure not only affects the diffusion pathways and increases access to larger molecules, but also influences the strength and concentration of acid sites, ion exchange properties, and the form and distribution of introduced metals. Modification of the latter properties may strongly increase the activity of redox sites in reactions involving inorganic molecules, such as nitrogen oxide selective catalytic reduction (SCR), selective catalytic ammonia oxidation (SCO), N_2O decomposition, and others.

The high potential of mesoporous zeolites is confirmed by numerous current review articles devoted to their synthesis, e.g., [1–7], their application in catalysis and adsorption in general [8,22,23], or in particular processes such as biomass conversion [24] or hydrocarbon oxidation reactions [25]. Despite the large amount of general scientific literature describing mesoporous zeolites, only a few reports focus on individual environmental catalysis reactions, bringing together the state of the art. Miao et al. [26] recently discussed the use of mesoporous zeolites in the catalytic elimination of air pollutants such as nitrogen oxides (focussing mainly on catalytic reduction of NO), volatile organic compounds, and carbon monoxide. Due to the lack of more detailed research on each of these types of pollutants, we would like to focus exclusively on the issue of nitrogen air pollutants such as NO_x , NH_3 , and N_2O , and their elimination through the use of mesoporous/hierarchical zeolites.

In this paper, we provide a brief review of the current state of the art in the catalytic activity of hierarchical zeolites in the conversion of nitrogen pollutants. The main objective of this review is to provide a summary of the investigated zeolite topologies and their modification methods, along with a critical assessment of the impact of the hierarchical porous structure on their catalytic properties.

Table 1. Review of the most popular methods for hierarchical zeolite preparation.

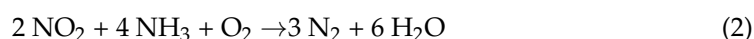
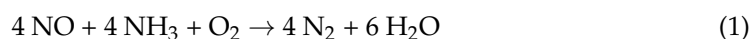
Short Description	Treatment/Synthesis Conditions	Remarks	References
Removal of the framework Si.	Treatment with organic or inorganic bases or a combination of both of them in strictly defined conditions (base concentration, process duration, and temperature).	It strongly depends on the Si/Al ratio. Partial amorphisation and crystallinity drop can be observed. Results in a wide pore size distribution. This may lead to Al debris on the surface of the zeolite that can be removed by subsequent acid treatment ('acid wash'). Simple and cheap.	[27–30]
Removal of framework Al.	Steam treatment (at temp. > 500 °C), acid treatment (also in combination with microwave irradiation), or heat treatment for strictly defined conditions (acid concentration, process duration, and temperature).	Partial amorphisation and crystallinity drop can be observed. Results in a wide pore size distribution. Increases the stability of zeolite steam/heat stability. The steam treatment causes the deposition of extra-framework Al species on the zeolite surface, which can be removed by subsequent acid treatment ('acid wash'). Simple and cheap.	[29–31]
Partial dissolution of zeolite and recrystallisation.	Dissolution in alkaline media or alternatively depolymerization with glycerol, followed by recrystallisation under hydrothermal treatment in the presence of meso-directing surfactant.	Zeolite crystals are embedded in the walls of the mesoporous material. Strong zeolitic acidity can be preserved.	[15,32,33]
Delamination or pillaring.	Expansion of the space between layers by additional surfactants and modification of the alignment of sheets by delamination (acidification and ultrasound treatment) or pillarization (e.g., SiO ₂ , TiO ₂ , or Al ₂ O ₃ pillars).	It can be applied only to layered zeolites. Mesopores are generated between the stacked layers. Demanding, laborious, with few step modifications.	[34–36]
During the synthesis, despite the zeolite SDA, a second template of mesopores is also used.	Addition of a soft mesopore template during zeolite synthesis, such as surfactants, polymers, and organosilanes.	Known also as the dual-template method. The mesopore template is removed by calcination. Often, specially designed templates (not available commercially), make the process complex and costly.	[37–39]
The zeolitic phase crystallises around the hard (solid) template (porogen).	Addition of a hard mesopore template (e.g., silica, carbon, starch, and polystyrene) in the form of particles, fibres, or nanotubes.	Known also as the dual-template method. Easy control of mesopore sizes. The hard template has to be removed by dissolution, burning (often requires high temperatures), or consumed during the synthesis.	[39–42]
Crystallisation under controlled conditions.	Self-assembly of crystals to create a mesoporous structure under controlled conditions of the nucleation, crystal growth, and aggregation stages.	Easy, one-step synthesis method without the use of mesopore structure-directing agent (SDA), which makes it economically and environmentally friendly.	[39,42–45]

Table 1. Cont.

Short Description	Treatment/Synthesis Conditions	Remarks	References
Size of the zeolite crystals in the nanometric range.	Synthesis of nanocrystals with the use of zeolite size-confining methods (seed-induced methods, use of microwaves, or ultrasonic irradiation), or reduction in the crystal size by milling.	Superior properties are characteristic of nanomaterials resulting from the high ratio between the external surface area of grains and their volume (short diffusion paths, enhanced accessibility to active sites, etc.).	[46,47]
Recrystallisation of mesoporous material in the presence of zeolite SDA.	Hydrothermal treatment of mesoporous material in the presence of a micropore structure-directing agent (SDA).	The risk of mesopore network collapse and formation of single zeolite crystals.	[32,48–50]
Thin zeolitic shell surrounding a hollow core.	Zeolitic shells can be prepared by the assembly of nanozeolites on a macrotemplate (e.g., polymer beads or mesoporous silica spheres), followed by hydrothermal and thermal treatment.	The size of macropores can be modified depending on the diameter of the macrotemplate. The mechanical stability depends on the thickness of the zeolitic shell.	[51–53]
Application of 3D printing technology to construct hierarchical zeolites.	Formation of hierarchical zeolite by 3D printing technology without the use of a binder.	Precise control of connectivity, proportion, and distribution of micro- and mesopores.	[54–56]

2. Selective Catalytic Reduction of NO_x with Ammonia (NH₃-SCR)

Nitrogen oxides (NO_x), such as NO and NO₂, are dangerous air pollutants that contribute to photochemical smog, ozone depletion, and acid rain. Despite environmental concerns, NO_x are also harmful to human health, and therefore studies on the reduction of NO_x emissions have been conducted in recent decades. Commercial catalysts for the selective catalytic reduction of NO_x with ammonia (NH₃-SCR, Equations (1) and (2)) are based on the metal oxide systems V₂O₅–WO₃–TiO₂ and V₂O₅–MoO₃–TiO₂. Several disadvantages of these catalysts (such as the narrow operating temperature range, the high volatility and toxicity of V₂O₅, WO₃, and MoO₃, and relatively high cost) are a driving force for studies of the new catalytic systems for NH₃-SCR [57,58]. Among the various material types considered as potential replacements for V-based catalysts, metal-exchanged zeolites are among the most promising. Their high activity in a broad temperature range and good thermal stability resulted in the commercialisation of Cu-SAPO-34 and Cu-SSZ-13 as diesel engine catalysts [59]. The disadvantages of zeolites as NH₃-SCR catalysts are related to the presence of micropores, which can be blocked relatively quickly by the deposition of byproducts under the reaction conditions, e.g., (NH₄)₂SO₄ or NH₄NO₃, resulting in increased internal diffusion limitations and reduced overall reaction rate. Generation of the secondary pore system may be crucial to overcome these difficulties, which, in turn, impacts the form of the introduced metal active in NO_x reduction (the presence of mesopores favours a better distribution of metal species).



Studies on hierarchical zeolite activity in NH₃-SCR revealed a high potential for topologies of CHA (SSZ-13, SAPO-34), MFI (ZSM-5), and BEA (Beta), modified mainly with Cu, Fe, or Mn [60]. In the case of Cu-modified zeolites, the most catalytically active species in NH₃-SCR are considered monomeric copper ions, which transform NO into N₂ [61]. On the contrary, CuO clusters promote NO oxidation to NO₂ at low temperatures [62], while at high temperatures, CuO clusters promote NH₃ oxidation to NO [63]. In the case of iron-modified zeolites, the activity of different Fe species depends on the reaction temperature. Isolated Fe³⁺ ions are recognised as the active iron form at temperatures < 300 °C. Between 300–500 °C, the oligomeric species of Fe_xO_y accelerate the reaction, while Fe₂O₃ oxide > 500 °C [64,65]. Thus, the high iron reducibility favours the adaptation of the active sites to the reaction conditions of NH₃-SCR toward N₂ and H₂O [60]. Therefore, the catalyst activity directly depends on the form of the active species and the method used for their deposition, which seems to be crucial for its application in NH₃-SCR. Modification of the porous structure of zeolites strongly influences their ion exchange properties, accessibility of acid sites, distribution, and form of introduced metal species. This is why studies of the activity of hierarchical zeolites in NH₃-SCR have gained great scientific interest.

Various methods were used for the generation of hierarchical porous structures in zeolites in order to increase their catalytic efficiency in NH₃-SCR. Desilication can be mentioned as the first one, due to its simplicity and low costs. Oord et al. [66] investigated the activity of Cu-SSZ-13, desilicated by NaOH solution at different concentrations. Cu-SSZ-13 disilicate with 0.1 M NaOH solution was found to show much higher NO conversion compared to conventional zeolite, especially at low temperatures, <200 °C (Figure 1). The observed increase in the hierarchical sample activity was connected to the generated mesoporosity (decreased diffusion limitations) with simultaneous preservation of intrinsic zeolitic properties. On the contrary, treatment of zeolite with more concentrated NaOH solutions decreased their catalytic activity. This effect was explained by a lower amount of Brønsted acid sites and a reduced pore volume of modified zeolites. Therefore, optimisation of desilication conditions (leaching agent concentration, duration, and temperature) has a strong impact on hierarchical zeolite activity in NH₃-SCR. Rutkowska et al. [67] investigated

the influence of desilication conditions with the use of NaOH and the NaOH/TPAOH (tetrapropylammonium hydroxide) mixture on Cu-ZSM-5 zeolite activity. In these studies, different desilication durations (1, 2, 4, and 6 h) and various TPA^+/OH^- ratios (0.2, 0.4, 0.6, 0.8, and ∞) were examined. The use of the so-called pore-directing agent in the form of quaternary ammonium cations aims to reduce the strong leaching effect of desilication with a significant decrease in microporosity, resulting in better preserved intrinsic zeolitic properties [68]. The best hierarchy factor (HF), which is used to assess the relationship between the generated mesoporosity and the preserved microporosity of the modified zeolite, was obtained for the TPA^+/OH^- ratio of 0.2 and the sample treated for 2 h. Cu-ZSM-5 samples modified by desilication showed increased activity in NO reduction with NH_3 , which was associated with increased acidity of the samples and a greater amount of copper introduced by the ion exchange method. Moreover, the reducibility of copper in the hierarchical samples was improved, which has a direct impact on the catalytic activity.

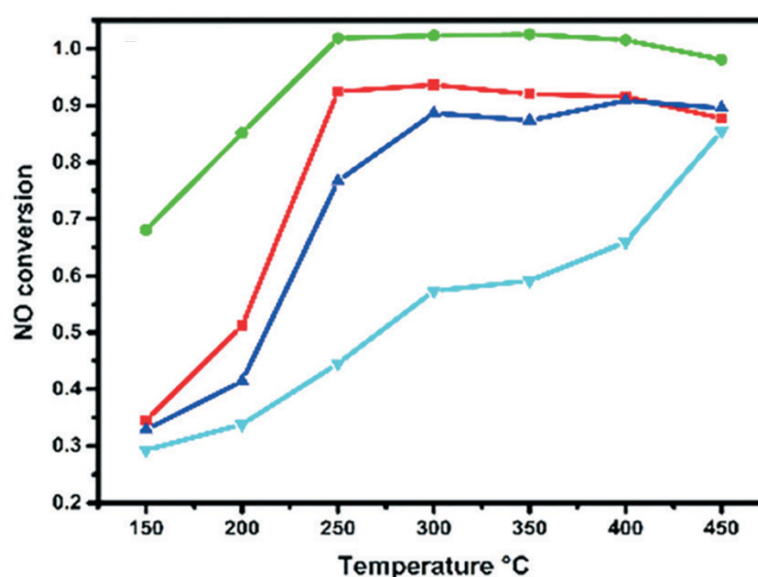


Figure 1. NO conversion over conventional Cu-SZZ-13 (red) and desilicated samples with different concentrations of NaOH (0.10 M (green), 0.15 M (dark blue), and 0.20 (cyan)). Reprinted with permission from Ref. [66]. Copyright 2017 Royal Society of Chemistry.

The impact of alkaline treatment of ZSM-5 with NaOH, which results in the generation of a hierarchical porous structure, on catalytic activity in NH_3 -SCR was also studied by Ma et al. [69]. After desilication, the samples were Fe exchanged by impregnation with $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$. The mesoporosity generated in the range of 2–20 nm improved the catalytic activity of the samples by increasing the concentration of Brønsted acid sites and the surface dispersion of iron. Furthermore, alkaline treatment of ZSM-5 prior to ion exchange was found to favour the formation of isolated Fe^{3+} ions and inhibit the sintering of iron in bulky iron oxide.

Zhang et al. [70] proposed an interesting catalyst for NO_x reduction based on a core-shell structure containing hierarchical SSZ-13. In the first step, the catalyst core was prepared by desilication of SSZ-13 with a 0.1 M NaOH solution. In a second step, the mesopore directing agent, P123, was added to the reaction mixture and, under controlled conditions (pH, temperature), silica and alumina (leached from zeolite during desilication) formed a mesoporous aluminosilicate (MAS) shell on the surface of the zeolite grains by self-assembly. In the next step, the sample was modified with copper by ion exchange using a solution of $\text{Cu}(\text{CH}_3\text{COO})_2$. The schematic representation of the core-shell meso-Cu-SSZ-13@MAS catalyst preparation with a hierarchical SSZ-13 core is presented in Figure 2. For comparison, conventional Cu-SZZ-13 and desilicated meso-Cu-SSZ-13 were also investigated and it was found that both desilicated and core-shell catalysts exhibited better activity

in comparison to classical zeolite. The observed improvement in catalytic efficiency was attributed to the mesoporosity generated by desilication. On the one hand, modification of the porous structure improved the internal diffusion of reactants, especially for small-pore SSZ-13 zeolite (pore openings ~ 3.8 Å). These assumptions have been confirmed by the kinetic calculations of apparent reaction activation (E_a), which for meso-SSZ displayed the highest value, indicating the smallest diffusion limitations among the examined samples. On the other hand, the modified porous structure affected the distribution of the deposited copper species, shifting them into monomeric Cu^{2+} ions, which are recognised as active sites of NH_3 -SCR. Moreover, it was found that the core-shell meso-Cu-SSZ-13@MAS catalyst is more stable under hydrothermal treatment conditions and more resistant to propene poisoning than conventional Cu-SSZ-13. Under hydrothermal treatment conditions, the Cu zeolite catalysts of NH_3 -SCR undergo deactivation by dealumination and deactivation of Cu species, which can result in the formation of CuAlO_x species. In the case of core-shell catalysts, the mesoporous shell effectively prevents the zeolitic core from being destroyed by dealumination, improving the catalyst's hydrothermal stability. On the other hand, catalyst deactivation by coke deposits in the presence of propene was reduced by much lower surface acidity in the case of the MAS shell compared to the conventional Cu-SSZ-13 catalyst with strong acid sites catalysing propene oxidation.

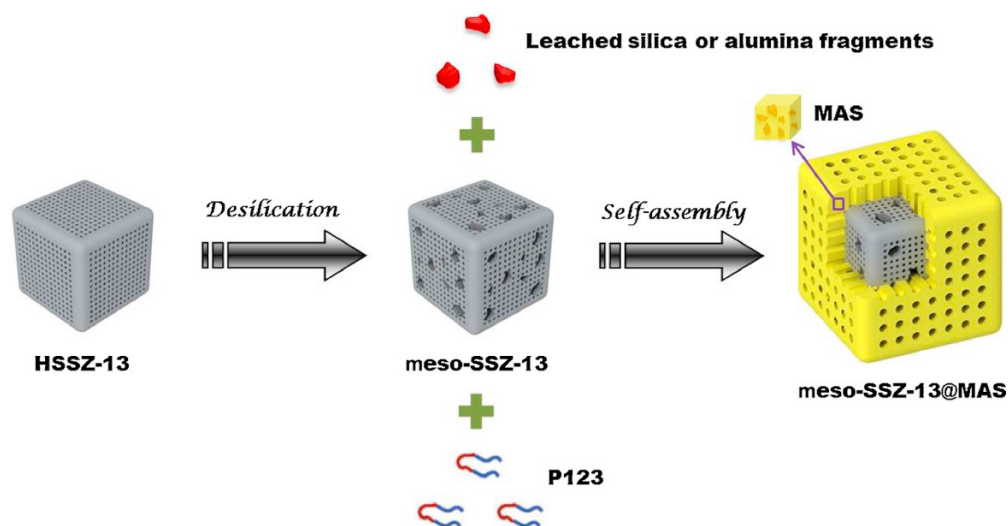


Figure 2. Schematic representation of the synthesis of the core-shell catalyst for NH_3 -SCR. Reprinted with permission from Ref. [70]. Copyright 2016 Elsevier.

Another interesting group of hierarchical zeolites examined in NO reduction with ammonia are the samples prepared by the soft-templating method. Liu et al. [71] investigated the activity of micro-mesoporous Cu-SAPO-34 prepared by one-step synthesis using the Cu complex with tetraethylenepentamine (TEPA). Hierarchical Cu-SAPO-34 was found to be more active than conventional microporous zeolite. This effect was explained by enhanced redox properties and improved accessibility to active sites as a result of the formation of mesopores. Kinetic studies showed that the mesopores generated in Cu-SAPO-34 reduce diffusion limitations and calculated values; the effectiveness factor ($\eta = 0.98$) or the effective diffusivity ($D = 10^{-9} \text{ m}^2/\text{s}$) demonstrated improved access of reactants to active sites. Peng et al. [72] compared the catalytic activity of conventional Cu-ZSM-5 and the hierarchical analogue prepared by one-pot synthesis with the use of a bifunctional organic template of the bola form. It was found that despite the improved catalytic activity, hierarchical zeolite also showed excellent hydrothermal stability and sulphur resistance. The enhanced activity, observed for Cu-ZSM-5-meso, was related to a greater specific surface area and surface acidity for NO and NH_3 adsorption and activation, as well as a better redox ability of Cu species.

As mesopore templates, despite “soft” organic molecules, “hard” substances can also be used. Wang et al. [73] applied CaCO_3 during one-step synthesis to produce hierarchical Cu/SAPO-34. The porogen was removed after the synthesis with the use of a 0.2 M solution of HCl. This relatively easy and economically viable synthesis (introduction of copper also occurred at the synthesis step, with the use of cupric citrate) resulted in a hierarchical catalyst that showed superior activity in NO reduction (high activity in a wide temperature range of 160–500 °C). Furthermore, this high activity was preserved even after severe hydrothermal treatment (10% H_2O , 700 °C). Li et al. [74] described similar findings for hierarchical SAPO-34 (Figure 3) prepared by templating with CaCO_3 and modified with copper by an additional step of ion exchange. In the case of this series of hierarchical catalysts, the operating window was also very broad, approximately 150–470 °C, and the resistance to the presence of H_2O and SO_2 in the reaction mixture was very high. The authors indicated an important influence of the hierarchical porous structure on the catalytic activity of SAPO-34 modified with copper in NH_3 -SCR.

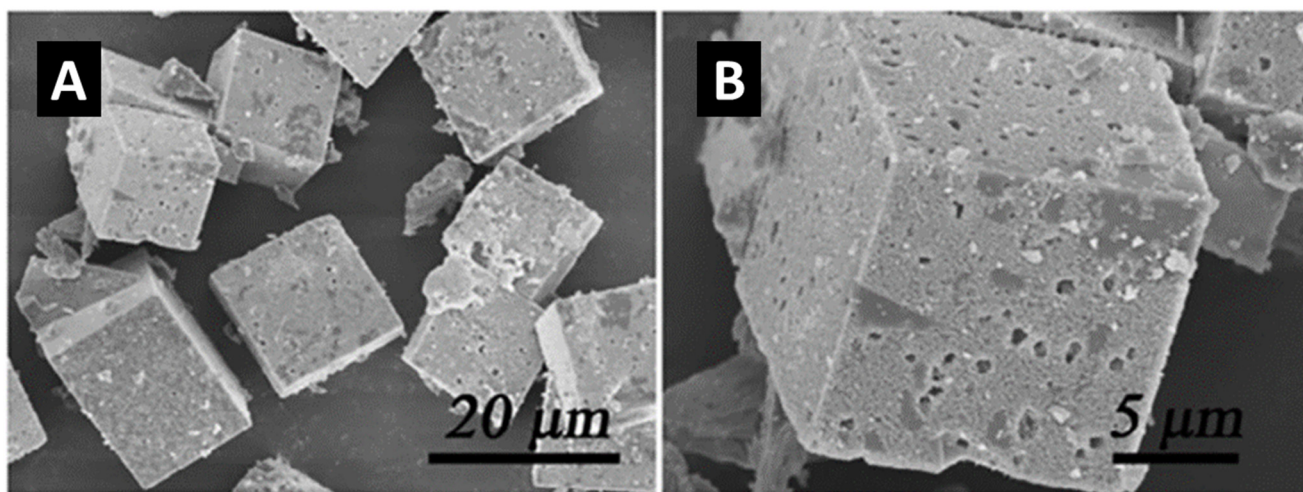
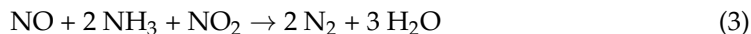


Figure 3. SEM images of hierarchical SAPO-34 prepared by the hard-templating method with the use of CaCO_3 as a porogen at lower (A) and higher magnifications (B). Reprinted with permission from Ref. [74]. Copyright 2020 Elsevier.

Liang et al. [75] used another type of hard matrix, carbon black, to create mesoporosity in Cu-SSZ-13. The obtained material was characterised by high crystallinity and the presence of mesopores and showed higher performance at low temperatures compared to conventional Cu-SSZ-13. The authors confirmed the improved transport of reactants and products in Cu-SSZ-13-Meso by mass transport calculations. Furthermore, using the in situ DRIFTS method, the higher resistance of mesoporous Cu-SSZ-13 to the formation and deposition of NH_4NO_3 and its better performance in the presence of SO_2 were determined.

One of the novel trends in the modification of zeolites is related to layered, so-called 2D zeolites. By modification of layer alignment, through delamination or pillaring, mesopores in the interlayer space can be created. This ability of 2D zeolites was used by Świąś et al. [76] to produce micro-mesoporous zeolites originating from ferrierite (FER)—ITQ-6 (delaminated) and ITQ-36 (silica-intercalated) modified with copper by ion exchange. Such modified zeolites were found to be effective catalysts of NO conversion with ammonia in a broad temperature range (250–400 °C), which was much wider compared to conventional 3D Cu-FER zeolite. The increase in catalytic activity was connected to the high dispersion of copper in modified zeolites, present mainly in the form of monomeric cations and small oligomeric species. These forms of copper were found to be more catalytically active than aggregated copper oxide species (present in conventional Cu-FER) in NO oxidation to NO_2 . The presence of NO_2 plays an important role in the mechanism of the so-called

fast SCR (Equation (3)), which is one of the possible pathways of the low-temperature NH_3 -SCR process.



The stability of the hierarchical Cu-ITQ-6 sample was examined in a continuous test at 275 °C for 15 h (Figure 4). It was found that the changes in NO conversion and selectivity to N_2 did not exceed 3%. Therefore, it can be concluded that zeolites with a hierarchical porous structure based on FER are not only active but also stable catalysts for NO reduction with NH_3 .

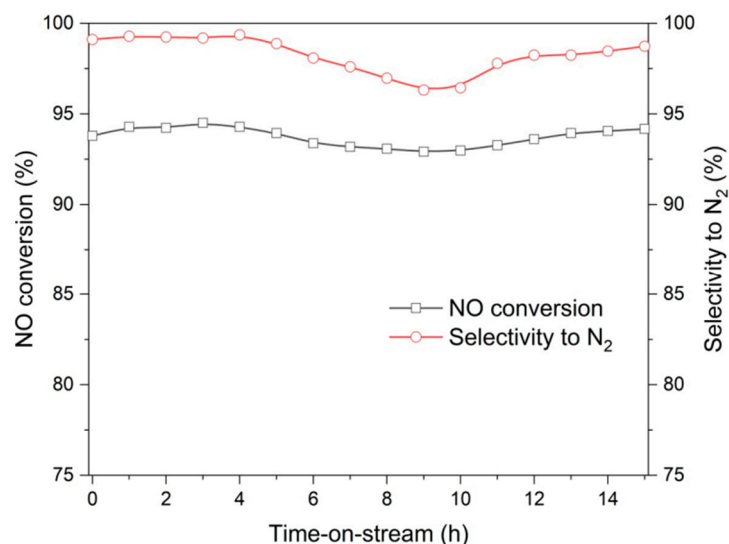


Figure 4. Stability NH_3 -SCR test at 275 °C of hierarchical ITQ-6 zeolite. Reprinted with permission from Ref. [76]. Copyright 2020 MDPI.

The stability of hierarchical zeolites obtained by modification of layered zeolites in NH_3 -SCR was also examined in terms of hydrothermal treatment [77]. In this case, the studies were concerned with another layered zeolite, MCM-22 (MWW topology). Copper-modified Cu-MCM-22 and its mesoporous derivative obtained by desilication, Cu-ITQ-2, were treated in a water vapour atmosphere at 550 °C for 3 h. The catalytic activity of the samples after treatment under such severe conditions did not change significantly (Figure 5). Only the competitive NH_3 oxidation process seems to be more preferential at high temperatures for the samples aged in a water–vapour atmosphere. This means that modification of the alignment of the layers in MCM-22 and the generation of mesoporosity do not decrease its stability and resistance ability against severe conditions.

An interesting spherical morphology of hierarchical FeCuZSM-5 was obtained in a one-step synthesis method under controlled conditions by Yue et al. [78]. The material obtained consisted of rod-shaped crystals, stacked in 5–10 μm spheroidal grains of 5–10 μm with intercrystalline mesoporosity (Figure 6). Bimetallic Fe-Cu catalysts have recently been in the spotlight of scientific interest due to the synergic effect of high copper activity at low temperatures (<300 °C) and superior iron activity at high temperatures (>300 °C). Hierarchical FeCuZSM-5 was found to show better catalytic performance in NH_3 -SCR compared to conventional Fe/ZSM-5, Cu/ZSM-5, and Fe/Cu/ZSM-5 obtained by the impregnation method. This superior activity was related to the higher amount of isolated Fe^{3+} and Cu^{2+} cations in the hierarchical sample.

A review of the literature on the activity of hierarchical zeolites in the selective catalytic reduction of NO with ammonia allows us to conclude that this topic is currently of great interest to scientists. A summary presenting the investigated zeolite types, methods of their modification to generate mesoporosity, and the most important findings concerning their activity in NH_3 -SCR is shown in Table 2. A large number of research reports have been related to zeolites: SSZ-13, SAPO-34, and ZSM-5, mainly modified with copper, and

as the most popular modification method, can be chosen for desilication. In general, the activity of hierarchical zeolites was similar to or even higher than that of their conventional counterparts. Porosity modification improved the metal dispersion and redox properties. Hierarchical catalysts also showed good resistance to H_2O and SO_2 poisoning/deactivation. Therefore, it seems that the potential for application of hierarchical zeolites in NH_3 -SCR is very promising, and more research is needed on this topic considering its large-scale synthesis and long-term activity/stability.

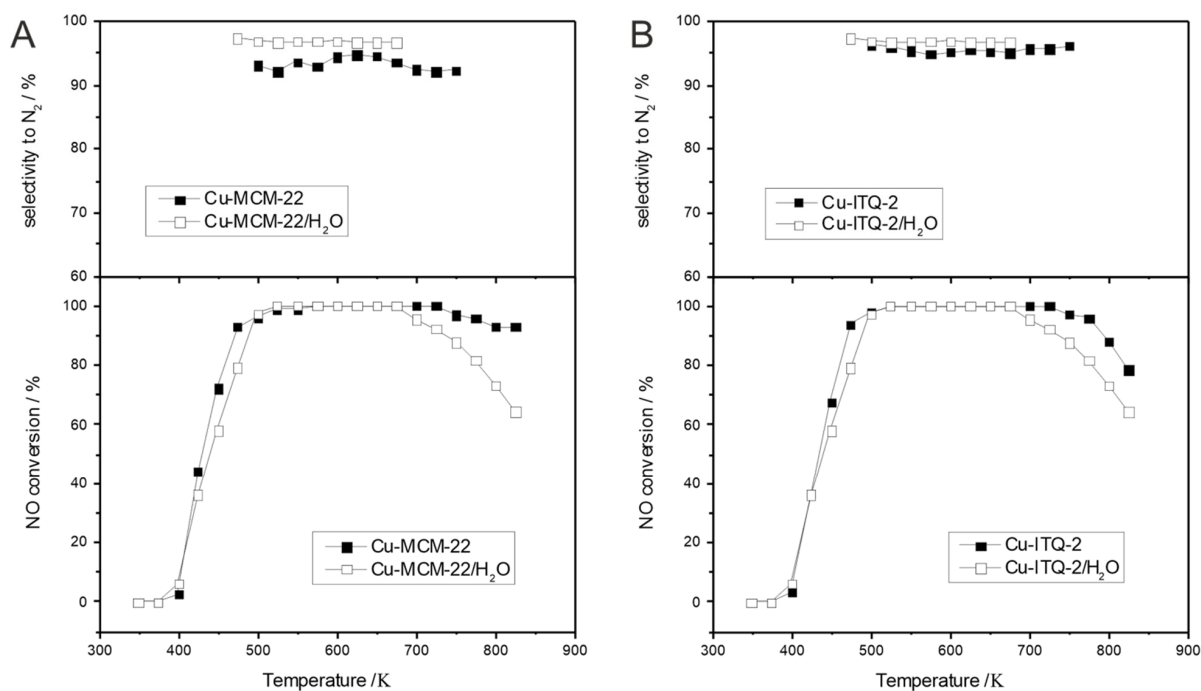


Figure 5. Comparison of the activity of the samples in NH_3 -SCR, fresh and after treatment in a water vapour atmosphere at 550°C for 3 h. The results for conventional Cu-MCM-22 (A) and its mesoporous derivative, Cu-ITQ-2 (B). Reprinted with permission from Ref. [77]. Copyright 2015 Elsevier.

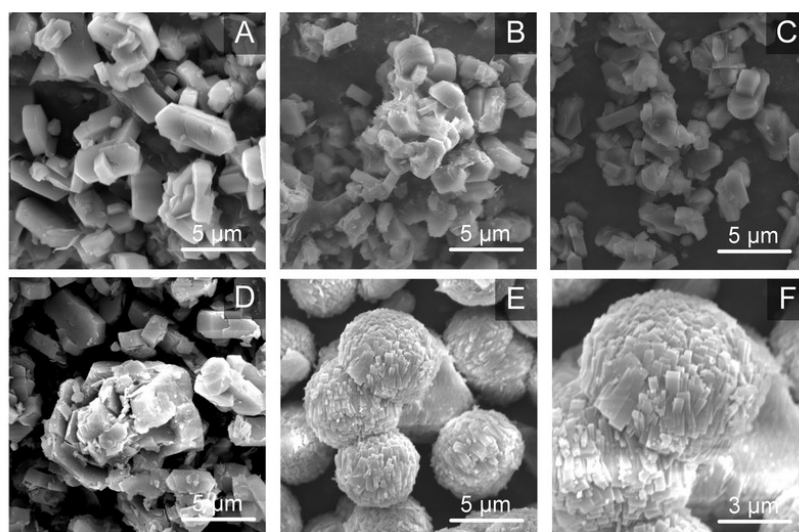


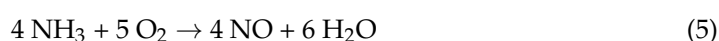
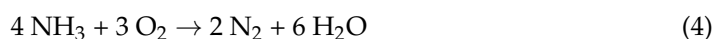
Figure 6. Morphology of conventional ZSM-5 (A) modified by impregnation with Cu (B), Fe (C), and Fe/Cu (D) and the hierarchical spherical FeCu-ZSM-5 obtained by one-pot method (E,F). Reprinted with permission from Ref. [78]. Copyright 2019 Wiley-VCH.

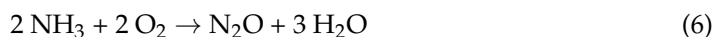
Table 2. Examples of the application of hierarchical zeolites as catalysts in NH₃-SCR.

Topology	Zeolite	Modification	Result	References
CHA	Cu-SSZ-13	Desilication	Increased activity, especially at low temperatures, <200 °C.	[66]
CHA	Cu-SSZ-13	Desilication/core-shell	Increased activity, high copper distribution, better hydrothermal stability, and resistance to propene poisoning.	[70]
CHA	Cu-SAPO-34	Soft-templating	Increased activity, enhanced redox properties, and improved diffusion.	[71]
CHA	Cu-SAPO-34 Cu-SSZ-13	Hard-templating	High activity in a broad temperature range, resistance to the presence of H ₂ O and SO ₂ and to NH ₄ NO ₃ formation. Improved reactant diffusion.	[73–75]
FER	Cu-ITQ-6 Cu-ITQ-36	Delamination/pillaring	Increased activity, high copper distribution, and very good stability.	[76]
MFI	Cu-ZSM-5	Desilication	Increased activity, higher surface acidity, higher amount of introduced Cu, and enhanced redox properties.	[67]
MFI	Cu-ZSM-5	Soft-templating	Increased activity, enhanced redox properties, better NO adsorption capacity, and good resistance for SO ₂ .	[72]
MFI	Fe-ZSM-5 FeCu-ZSM-5	Desilication, spherical (template-free)	Increased activity, high dispersion of iron. Iron and copper are mainly in the form of isolated cations Fe ³⁺ and Cu ²⁺ .	[69,78]
MWW	Cu-ITQ-2 Cu-MCM-36 Fe-ITQ-2	Delamination/pillaring	Higher activity of Cu-modified samples and very good hydrothermal stability.	[77]

3. Selective Catalytic Oxidation of Ammonia (NH₃-SCO)

Ammonia (NH₃) is one of the most important chemicals in industry. It is used to produce fertilisers, explosives, fine chemicals such as nitric acid, synthetic fibres, dyes, and many others. On the other hand, despite the numerous advantages of the use of this molecule, the release of ammonia into the atmosphere is very harmful to the environment. Ammonia is listed by the European Union as one of the four hazardous air pollutants, along with NO_x, SO₂, and no-methane volatile organic compounds [79]. Despite the main source of NH₃ emissions being agriculture, the rapidly increasing sources of ammonia emissions from industry are connected to the automotive and energy production sectors [80]. In the transportation sector, NH₃ slip is related to the use of three-way converters (in the case of gasoline cars) and diesel exhaust fluid (DEF) technology (in the case of diesel cars). DEF technology applies the urea solution as the ammonia source for the reduction of NO_x (so-called AdBlue solution) [80]. Among the possible methods to eliminate ammonia emission (membrane separation, biotreatment, adsorption, absorption, thermal combustion, or direct decomposition), the most environmentally friendly (also adaptable to reaction conditions and economically effective) is selective catalytic oxidation (SCO), leading to natural inert air components, N₂ and H₂O (Equation (4)) [81]. Ammonia oxidation may also result in undesired products, such as NO or N₂O (Equations (5) and (6)). Therefore, the selectivity to N₂ must be controlled by the properties of the catalysts used.





Different metal-based materials were tested in the NH_3 -SCO process, but three main types of catalysts can be mentioned as the most promising: noble metals (deposited on various supports, such as Al_2O_3 , TiO_2 , or SiO_2), modified zeolites, and metal oxides [80]. The advantages of zeolites over other types of catalysts are their uniform porous structure, strong surface acidity, and ion exchange properties, which enable high dispersion of active metals. Selective oxidation of ammonia to nitrogen over zeolites not modified with metals is reported to occur by internal selective reduction between nitrogen oxides obtained from direct ammonia oxidation and ammonia adsorbed on Brønsted acid sites. However, this reaction is possible only at high temperatures. The shift of the operation window to lower temperatures requires modification of zeolites with transition metals, such as Cu, Cr, Ag, Co, Fe, Ni, Mn, or Pd [80]. However, it seems that copper and iron-modified zeolites are the most promising ones. As active zeolite types in NH_3 -SCO, ZSM-5 (MFI), Y (FAU), Beta (BEA), mordenite (MOR), ferrierite (FER), SSZ-13 (CHA), and SAPO-34 (CHA) were reported [80,82]. The impact on the activity and selectivity of metal-modified zeolites in this reaction is related to the pore sizes (it seems that small and medium pore zeolites are responsible for better reaction selectivity to N_2 [82]) and to the content and dispersion of metal. This second factor can be influenced and tailored by modification of the porous structure of zeolites, namely the generation of mesoporosity.

Góra-Marek et al. investigated the influence of mesopore generation, especially in terms of surface acidity and the form of active species, on the activity of AgY [83] and Fe-ZSM-5 [84] in NH_3 -SCO using IR spectroscopic methods. In the case of zeolite Y [83], the authors compared the catalytic activity of conventional microporous AgY and mesoporous ultra-stabilised AgUSY. The effective catalytic operation of AgUSY started at a temperature about 100 °C lower than that for conventional AgY, with a stable selectivity to nitrogen of approximately 95% above 175 °C. This difference in catalytic performance of conventional and mesoporous catalysts was related to the different dispersion of Ag. In the case of AgUSY, STEM analysis revealed a more uniform distribution of Ag species and smaller silver aggregates than in the case of classical AgY (small particles of Ag^0 are responsible for activity at low temperatures, <140 °C). The silver state in both samples was examined by IR studies of the CO pre-sorbed samples (Figure 7). In the case of AgUSY, the bands corresponding to monocarbonyls interacting with Ag^+ (2199 and 2189 cm^{-1}) are shifted to higher frequencies in comparison to AgY (2194 and 2175 cm^{-1}), which can be correlated with different electronegativity of the zeolite framework (lower Si/Al ratio after dealumination), related to better electron acceptor properties. In the case of AgUSY, a higher amount of Ag^0 was also detected (band at 2160 cm^{-1}), which can be connected to a more efficient reduction of Ag^+ by the USY framework with lower electronegativity. These properties, namely the strong electron acceptor properties of Ag^+ present in AgUSY, can be related to the high reaction selectivity toward N_2 (protection against oxidation of ammonia chemisorbed in Ag^+ cations). Furthermore, the activity and selectivity of the AgUSY catalyst tested in the presence of water vapour and CO_2 , and during the long-term stability test in the presence of water vapour, did not change practically.

The second type of zeolite investigated by Góra-Marek et al. [84], hierarchical ZSM-5, was prepared by two methods: desilication with the mixture of NaOH and TBAOH (tetrabutyl ammonium hydroxide) and direct synthesis with a mesopore-directing agent, using amphiphilic organosilanes as a soft template. Both types of hierarchical ZSM-5 were modified with iron by ion exchange with a $\text{Fe}(\text{NO}_3)_3$ solution. Mesoporous materials exhibited higher activity in NH_3 -SCO compared to conventional microporous Fe-ZSM-5, with simultaneous very high selectivity to N_2 . The authors related this enhancement to the different nature of Fe species present in the studied catalysts. In the case of hierarchical Fe-ZSM-5, iron was present mainly in the form of tetrahedral Fe(III), while in the case of conventional iron-modified ZSM-5, a high contribution of oligomeric iron oxide clusters

and Fe_2O_3 species was detected. Moreover, the presence of mesopores could have an impact on the internal diffusion of the reactants inside the pores.

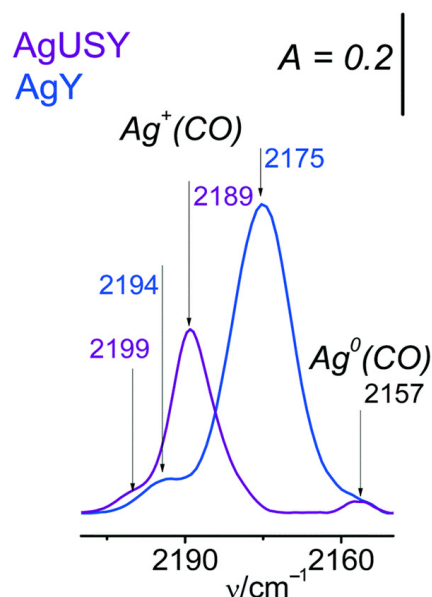


Figure 7. IR studies of CO adsorption (intensity of the $\text{Ag}^+(\text{CO})$ and $\text{Ag}^0(\text{CO})$ monocarbonyl bands) for AgY and mesoporous AgUSY zeolites. Reprinted with permission from Ref. [83]. Copyright 2016 Royal Society of Chemistry.

Ma et al. [69] tested mesoporous Fe-ZSM-5 prepared by desilication with the use of NaOH solution in two concentrations (0.4 M and 0.6 M). In these studies, the authors found mesoporous zeolites slightly less active than conventional microporous Fe-ZSM-5. This was related to the amount of oligomeric species, which was higher in the case of classical Fe-ZSM-5. It seems that the conditions of the desilication process (type of desilication agent, its concentration, duration, and temperature of treatment) have a strong impact on the final catalyst properties and activity in NH_3 -SCR. Rutkowska et al. [67] prepared a series of Cu-ZSM-5 catalysts desilicated with a mixture of NaOH and TPAOH (tetrapropyl ammonium hydroxide), with TPA^+/OH^- ratios equal to 0.2, 0.4, 0.6, and 0.8 and exclusively with NaOH for 1, 2, 4, and 6 h. They found that NH_3 -SCO in the case of hierarchical samples proceeded with significantly higher ammonia conversion (with simultaneous high selectivity to N_2 , greater than 90%), which was mainly related to the easier reducibility of copper species in a defected system of mesoporous materials. Figure 8 presents the results of the H_2 -TPR measurements for conventional microporous Cu-ZSM-5 and samples desilicated with NaOH and the mixture of $\text{TPA}^+/\text{OH}^- = 0.2$ for 1, 2, 4, and 6 h. In the case of the reference sample, three reduction steps were found in the reduction profile: $\text{Cu}^{2+} \rightarrow \text{Cu}^+$, $\text{CuO} \rightarrow \text{Cu}^0$, and $\text{Cu}^+ \rightarrow \text{Cu}^0$. In the case of hierarchical samples, only two reduction steps of Cu^{2+} and Cu^+ were observed, however, at lower temperatures than in the case of Fe-ZSM-5. This result suggests that copper species in conventional zeolite have a stronger tendency to agglomerate with CuO formation than modified mesoporous structures. Furthermore, the introduction of copper into disilicate samples resulted in better reducibility of the samples and, therefore, their catalytic activation in NH_3 -SCO.

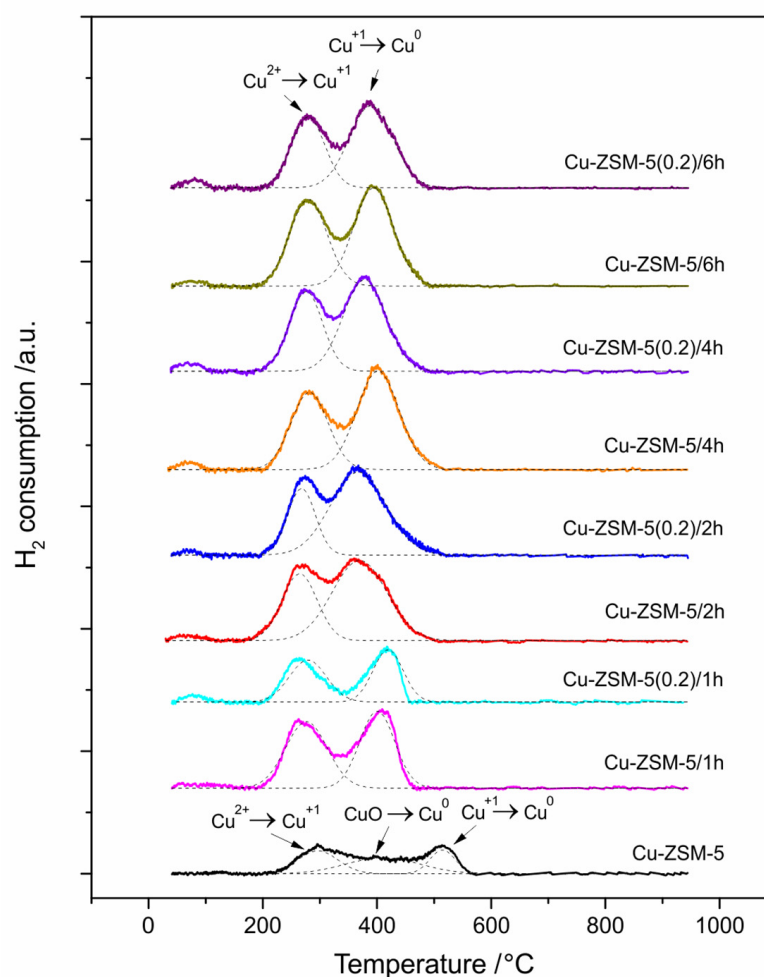


Figure 8. H₂-TPR profiles of the samples desilicated under different conditions and with reference to conventional Cu-ZSM-5. Reprinted with permission from Ref. [67]. Copyright 2017 Elsevier.

Not only do the conditions of the desilication process have a very important impact on the overall catalytic activity in ammonia oxidation, but the method used for the introduction of active metals into hierarchical zeolite also has an important impact. Borch et al. [85] compared the activity of conventional Fe-ZSM-5 (MFI topology) with desilicated analogous (mixture of NaOH and TPAOH, total concentration of OH[−] = 0.2 M, 4 h at 65 °C). The samples were modified with iron by ion exchange or by impregnation. Additionally, two sources of iron were used: FeSO₄·7H₂O, Fe²⁺ cations and trinuclear iron oligocations in the form of the [Fe₃(OCOCH₃)₇·OH·2H₂O]NO₃ complex (Fe₃). It was found that ion exchange with Fe₃ oligocations and impregnation (both with monomeric cations and oligocations) resulted in much more efficient catalysts than the samples containing mainly isolated Fe³⁺ cations deposited by the ion exchange method using a FeSO₄ solution (Figure 9). The presence of mesopores was beneficial only in the case of ion exchange with Fe₃ oligocations, probably due to improved diffusion properties (more open structure) resulting in a higher amount of deposited iron species. It is worth mentioning that the desilicated sample modified by ion exchange with Fe₃ oligocations showed very good stability in the conversion of NH₃ and selectivity to N₂ during the 60 h of the isothermal catalytic test.

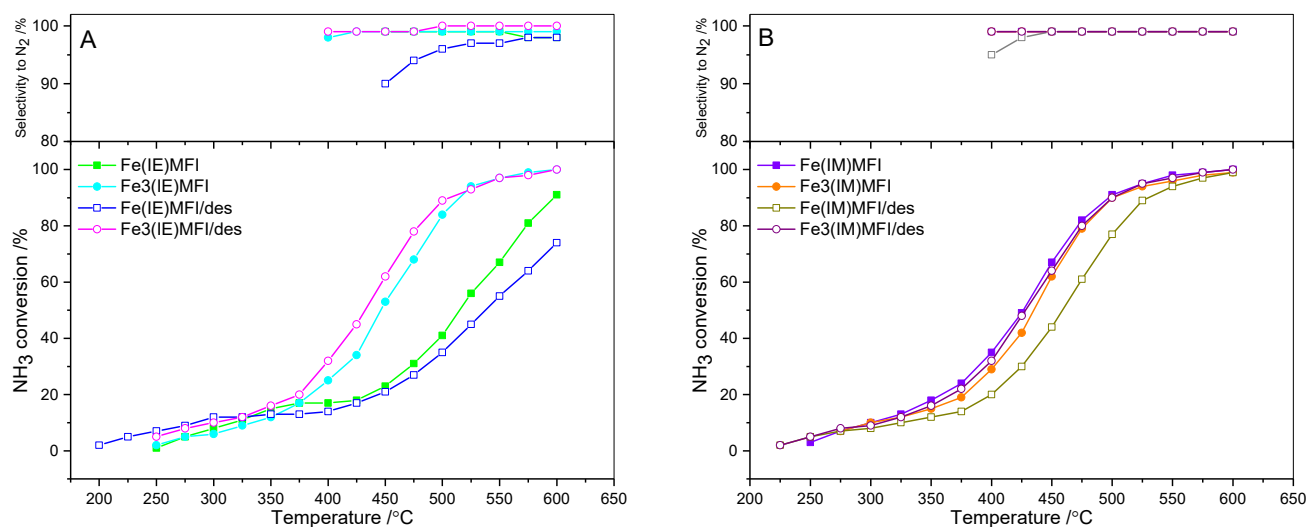


Figure 9. The results of the NH₃-SCO tests over conventional and desilicated MFI modified with FeSO₄ and Fe₃ oligocations by ion exchange (A) and impregnation (B). Reprinted with permission from Ref. [85]. Copyright 2020 Elsevier.

Trinuclear metallic aggregates were also used for the activation of mesoporous zeolite Beta in NH₃-SCO [86]. In these studies, mesopores in Beta zeolite were created in one synthesis step using the so-called mesotemplate-free method (assembly of zeolite crystals under controlled conditions). The differences in porosity and morphology between conventional and mesoporous Beta zeolite are shown in Figures 10 and 11, respectively. The applied synthesis method resulted in a material with bimodal porosity, characterised by nitrogen sorption isotherm of type IVa and hysteresis loop of type H4, which are typical of mesoporous material consisting of aggregated zeolite crystals with interparticle porosity. In the case of H-Beta/meso, the mesopores were in the range of 12–37 nm. FESEM morphology studies of the samples (Figure 11) show uniform grains of 200–400 nm size in the case of H-Beta. On the contrary, the grains of H-Beta/meso were less regular, ragged, and sharp, with a clear sponge-like structure. Modification of these samples with acetate complexes [Cr_{3-x}Fe_xO(OAc)₆·AcOH·2H₂O]NO₃ (where x = 0, 1, 2 or 3), called Fe₃, Fe₂Cr, FeCr₂, and Cr₃ oligocations, significantly increased their activity in NH₃-SCO. It should also be mentioned that modified samples with Fe₃ oligocations were more catalytically active than samples prepared by ion exchange with monomeric Fe cations. The highest activity among the materials examined showed the catalysts modified with the chromium-containing species in the following order Cr₃ > FeCr₂ > Fe₂Cr. It seems that the addition of iron positively influences the reaction selectivity to nitrogen, which proves the positive effect of the bimetallic system. Analysing the impact of the generated mesoporosity on the overall efficiency of the catalysts, a positive effect on NH₃ conversion can be assumed in the case of Cr-modified samples; however, a decrease in the selectivity of the reaction to N₂ was also observed. In the case of iron-modified samples, the mesoporous sample, Fe₃-Beta/meso, showed lower activity than the conventional Fe₃-Beta. Considering that the mesoporous structure favours a better distribution of metals in zeolites, the obtained results indicate that for the chromium-modified samples, isolated cations or small oligomers are more catalytically active than more aggregated chromium oxide species, while, in the case of iron, more aggregated species exhibit better activity in ammonia oxidation.

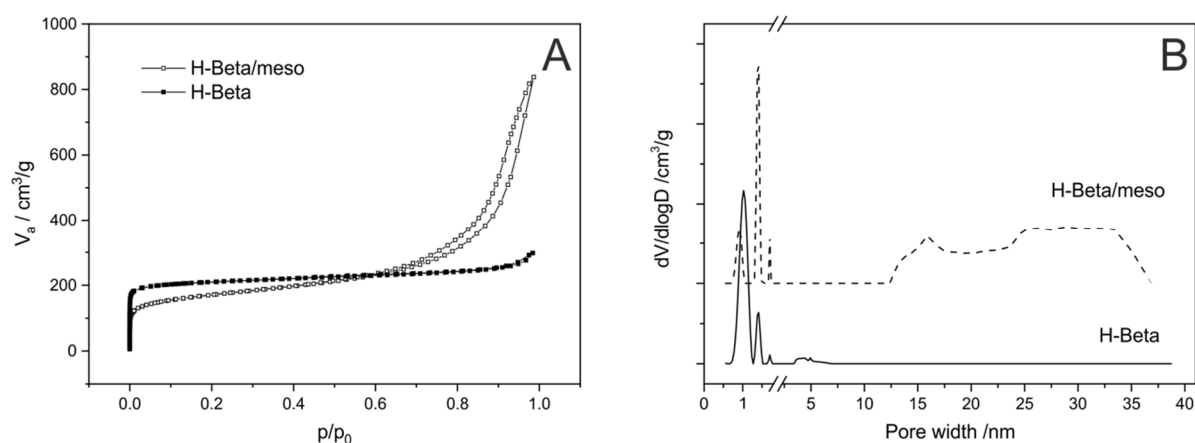


Figure 10. Nitrogen sorption isotherms (A) and pore size distribution (B) of conventional H-Beta and mesoporous H-Beta/meso zeolites. Reprinted with permission from Ref. [86]. Copyright 2019 Elsevier.

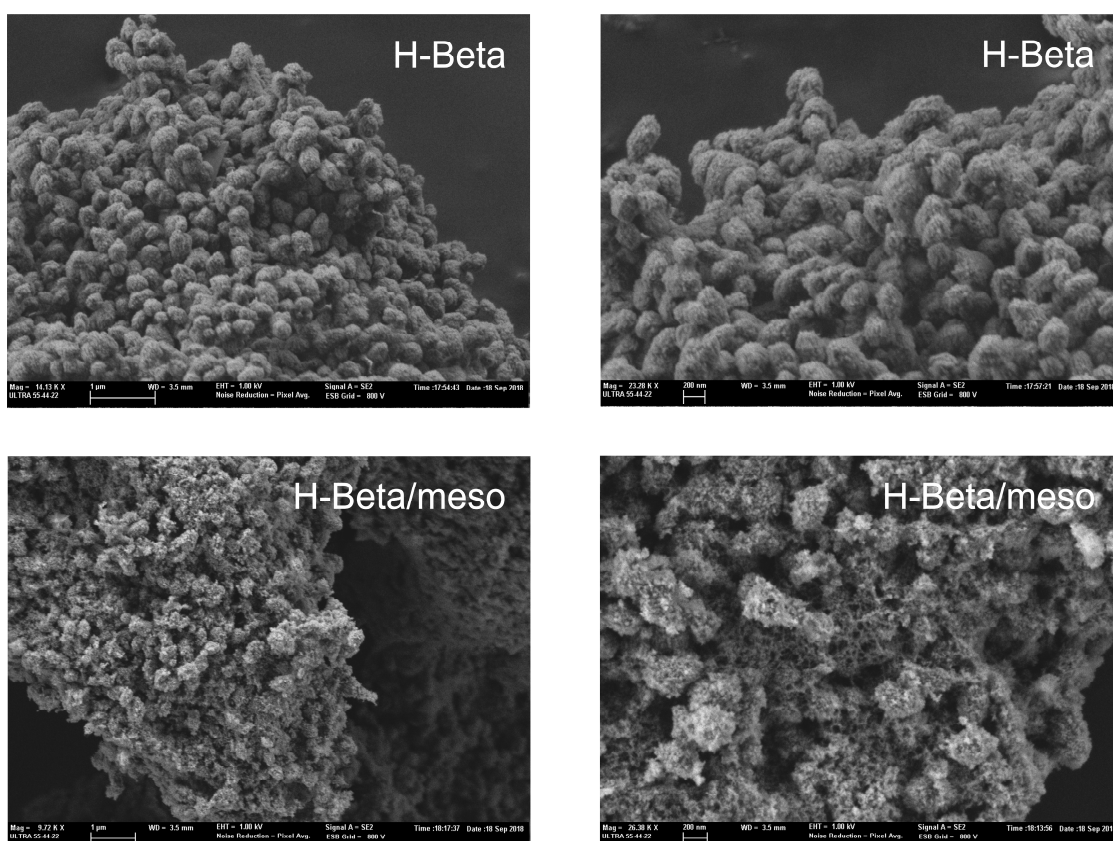


Figure 11. FESEM micrographs of conventional H-Beta and mesoporous H-Beta/meso zeolites. Reprinted with permission from Ref. [86]. Copyright 2019 Elsevier.

Despite the most popular demetallation method (desilication/dealumination) and the template-free method mentioned above, other interesting methods, such as the delamination of layered zeolites [87] or the synthesis of hollow zeolitic shells [88], were applied to improve the efficiency of NH_3 -SCO catalysts. Świąś et al. [87] studied the influence of the forms of active species and the morphology of zeolite on the efficiency of ammonia oxidation in the presence of ferrierite and its delaminated analogue, mesoporous ITQ-6. FER zeolites containing aluminium or titanium in the zeolite framework were modified with copper by the ion exchange method. The presence of Al in the samples resulted in highly dispersed copper cations that were highly stabilised at the ion exchange positions.

In the case of the Ti samples, the aggregated copper species were formed as a result of metal sintering under calcination conditions. On the other hand, it was found that for delaminated samples, a higher dispersion of copper was obtained compared to their conventional microporous counterparts. This effect was probably related to the improved accessibility of the ion exchange positions and improved internal diffusion in the mesoporous samples. The authors postulate that copper aggregates oxidise part of ammonia to NO, while monomeric Cu is active in NO reduction with residual ammonia to N₂ (so-called internal selective catalytic reduction, iSCR mechanism). Thus, the optimal ratio between these two forms of copper results in the improved conversion of ammonia and reaction selectivity to nitrogen. In this series of samples, the best catalytic properties are presented by Cu/Al-ITQ-2.

The application of hierarchical zeolites in NH₃-SCO was beneficial due to the better distribution of the metal, the enhanced reducibility, and the accessibility of the active species. Examples of different mesoporous zeolites tested in this reaction with the main results of the studies are presented in Table 3. The greatest interest in the investigation of hierarchical zeolite activity in NH₃-SCO has been focused on ZSM-5 zeolite (MFI topology) and desilication, as its modification method is the most widely used. In general, modification of the porosity of zeolite has a positive impact on catalyst activity and stability. However, in some cases, for example, for iron-modified ZSM-5 [69,86], the mesoporous sample was less active than the conventional one. This effect is possibly related to the increased activity of more aggregated oligomeric iron oxide species in the NH₃-SCO reaction. Thus, the high efficiency of zeolites in this reaction is affected by various factors, such as modified porosity, acidity, method of modification with metal, type of metal, and many others. However, it is clearly seen that the generation of hierarchical porosity in zeolites can have a positive impact on the final activity of the catalyst in the selective oxidation of ammonia to N₂.

Table 3. Examples of the application of hierarchical zeolites as catalysts in NH₃-SCO.

Topology	Zeolite	Modification	Result	References
BEA	Fe _x Cr _y -Beta	Template-free	Slightly increased activity in the case of Cr-modified samples with a simultaneous decrease in selectivity to N ₂ . Lower activity in the case of Fe-modified samples.	[86]
FAU	Ag-Y	Dealumination	Increased activity, better dispersion of smaller Ag particles, resistance to the presence of H ₂ O and SO ₂ , and good long-term stability.	[83]
FER	Cu-Al-ITQ-6	Delamination	Increased activity, high selectivity to N ₂ , high dispersion of copper species (good balance between monomeric and aggregated Cu species).	[87]
MFI	Ag-ZSM-5	Hollow	Better long-term stability and resistance against Ag sintering and leaching from the sample. Very good SO ₂ and H ₂ O resistance.	[88]
MFI	Fe-ZSM-5	Desilication	Increased activity, high dispersion of iron.	[84]
MFI	Fe-ZSM-5	Desilication	Slightly higher NH ₃ conversion, good stability during 60 h of catalytic reaction, and higher amount of introduced iron.	[85]
MFI	Fe-ZSM-5	Desilication	Lower activity and lower content of oligomeric iron species than in conventional zeolite.	[69]
MFI	Fe-ZSM-5	Soft-templating	Increased activity, high dispersion of iron.	[84]
MFI	Cu-ZSM-5	Desilication	Increased activity and surface acidity, better reducibility of copper species.	[67]

4. N₂O Decomposition

Another nitrogen gaseous air pollutant, N₂O, has a very harmful impact on the environment. The global warming potential (GWP) of this gas is about three hundred times higher than that of CO₂. Furthermore, N₂O depletes the ozone layer and has a very long lifetime in the atmosphere (estimated at approximately 150 years). The main sources of anthropogenic nitrous oxide emission are related to the chemical industry (e.g., production of adipic acid and nitric acid), utilisation of nitrogen fertilisers, and the combustion of fossil fuels. Various methods of N₂O emission reduction have been proposed, such as adsorption, thermal decomposition (at high temperatures, >600 °C), reduction (emission of other hazardous oxides such as CO₂ or SO₃), and photocatalytic or catalytic decomposition. Because of the cost and energy efficiency, the latest catalytic solution is considered to be the most effective. The catalytic decomposition of N₂O proceeds according to Equation (7), selectively resulting in environmentally neutral products such as nitrogen and oxygen [89].



Several groups of materials were examined as potential catalysts for this reaction, such as noble metals (e.g., Pt, Pd, Rh, and Ru) supported on oxides of high surface area (e.g., Al₂O₃, CeO₂, or mesoporous silicas), transition metal oxides (e.g., Co₃O₄, NiO, MnO₂, CuO, Fe₃O₄, mixed metal oxides, and spinels), or metal-exchanged zeolites [90]. Zeolites, such as ZSM-5, ZSM-11, Beta, Mordenite, USY, Ferrierite, and Chabazite (SAPO-34, SSZ-13 [91,92]) modified by the ion exchange method with Fe, Co, Ni, Cu, Mn, Ce, Ru, Rh, and Pd were found to be catalytically active in the decomposition of nitrous oxide. However, it seems that the greatest attention has been paid to Fe-ZSM-5 [89]. Modification of zeolite with iron results in a bifunctional acid–redox catalyst. In the case of zeolites, Lewis acid sites are generated by dehydroxylation of bridging ≡Si–O(H)–Al≡ groups (Bronsted site) at high temperatures. Additional modification of ZSM-5 with iron generates redox active sites. The vicinity of these two types of active sites increases the effectiveness of N₂O decomposition by improving oxygen recombination [93]. During N₂O decomposition, oxygen is adsorbed at active sites (Equations (8) and (9)), and its recombination and desorption from the catalyst surface (Equations (10)–(12)) is the stage that determines the rate of N₂O decomposition [89]. Therefore, catalysts that improve the oxygen desorption process are characterised by the highest efficiency in this reaction. It is important to note that the activity of the final catalysts depends on the type of zeolite, its acidity, concentration, and the form of iron introduced. In the case of iron, dispersed octahedrally coordinated Fe⁺³ ions show the highest activity. Similar findings were obtained in the case of Co-ZSM-5. In this case, isolated dispersed Co²⁺ cations were found to be more active than cobalt oxide aggregates [94]. The catalytic results obtained for conventional zeolites (higher activity of dispersed, isolated cations) suggest the potential attractiveness of hierarchically structured zeolites in N₂O decomposition. The open porous structure, the developed external surface area, and the modulated acidity may result in a better distribution of the catalytically active species.



Several studies have focused on mesoporous Fe-ZSM-5 zeolites prepared by desilication and their activity in the decomposition of N₂O. Different desilication conditions, such as 0.2 M NaOH solution, 80 °C, treatment for 30 and 120 min [95]; 0.2 M NaOH, 90 °C,

90 min [96]; and a mixture of NaOH and TPAOH (different TPA⁺/OH[−] ratios), 90 °C, 90 min [97] were applied to determine the influence of this modification method on their catalytic performance. Iron was introduced into desilicated zeolite samples by ion exchange with the use of Fe(NO₃)₃·9H₂O solution. The changes in the morphology and textural properties of ZSM-5 are intensified by extending the duration of the desilication process, as presented by Melián-Cabrera et al. [95] in Figure 12. In all cases, alkaline treatment had a positive effect on the catalytic activity of Fe-ZSM-5 in the decomposition of N₂O. Reduction in crystal size and generation of mesopores enabled complete ion exchange with Fe³⁺ (better accessibility to ion exchange positions) with the formation of only a negligible amount of FeO_x.

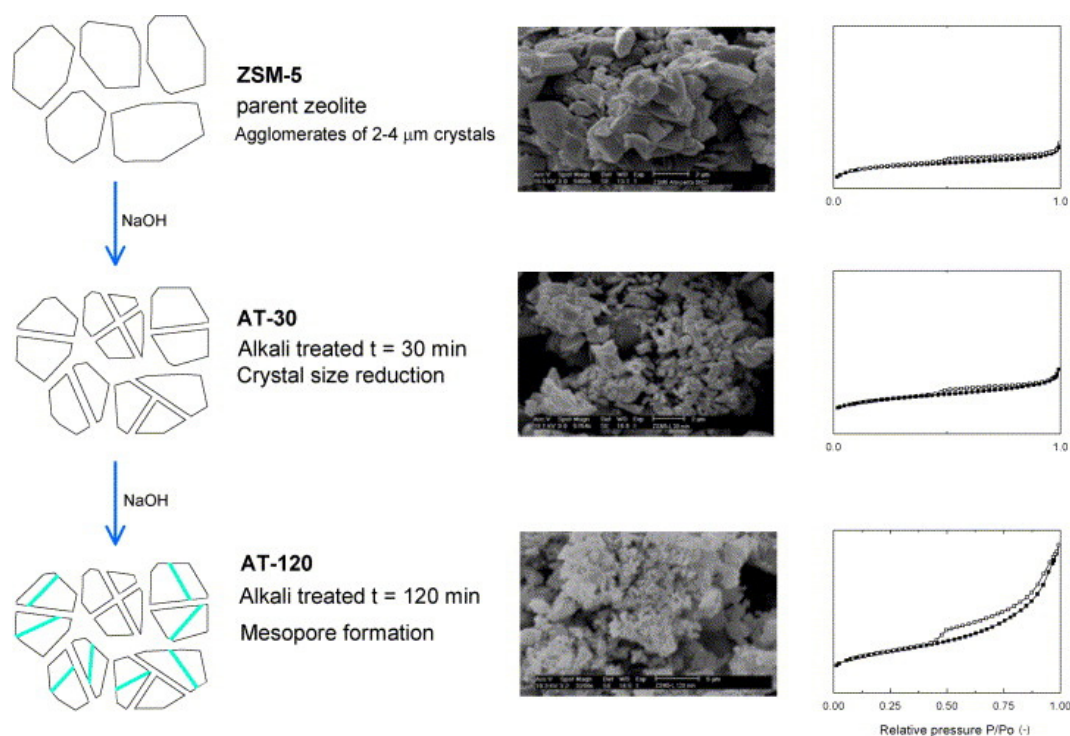


Figure 12. Changes in ZSM5 morphology after alkaline treatment for different durations. Reprinted with permission from Ref. [95]. Copyright 2006 Elsevier.

Another strategy was examined by Groen et al. [98]. In this case, a reverse order of desilication and ion exchange processes was applied. ZSM-5 zeolite was first modified by ion exchange with iron (II) sulphate solution and then by alkaline treatment with 0.2 M NaOH solution at 100 °C for 30 min. However, such treatment generated intracrystalline mesoporosity and an increased population of isolated Fe³⁺ cations, which finally resulted in the reduced catalytic activity of this sample in N₂O decomposition compared to conventional Fe-ZSM-5. What was interesting was that subsequent ion exchange of the alkaline-treated sample with NH₄NO₃ influenced iron speciation (leading to a composition similar to the parent zeolite, but with a higher Fe²⁺ concentration) and resulted in an improved N₂O decomposition activity of the sample. This effect was related to a higher concentration of Fe²⁺ cations that are responsible for the N₂O activation (the first step in N₂O decomposition) and better O₂ desorption (reaction rate-determining step). To create this type of iron species, both processes, desilication and ion exchange with an ammonium nitrate solution, are required. By such modifications of Fe-ZSM-5, both mesoporosity and iron form are altered, increasing the starting zeolite activity in N₂O decomposition.

Similar results were obtained in the case of Fe-ZSM-5 modification by one-pot solvothermal synthesis [99] and by the soft template method [100]. The first method resulted in the samples with the structure of the nanoflower sheets. The samples were characterised by

high specific surface area and volume of pores. The activity of the mesoporous samples was compared with that of commercial zeolite, and their higher efficiency was ascribed to the improved diffusion and higher iron loading. The latter method, with the use of 3-aminopropyltriethoxysilane (APTES) in the synthesis system, resulted in the spherical morphology of ZSM-5 zeolite with intercrystalline mesoporosity. The modified synthesis method resulted in greater catalytic activity in the N_2O decomposition of the final iron-modified spherical Fe-ZSM-5 compared to conventional zeolite.

Pérez-Ramírez et al. [101,102] investigated the catalytic activity of various forms of iron species in ZSM-5 in the decomposition of N_2O . It was shown that tetrahedral framework iron cations, inactive in N_2O decomposition, can be activated by steaming under controlled conditions. When the temperature and partial steam pressure are adjusted, an optimum content of isolated extra-framework iron cations and small oligomeric species can be generated in the sample (without the formation of highly aggregated iron oxide particles). Furthermore, post-steam alkaline treatment additionally improved catalyst activity by mesopore formation and improved mass transport.

The positive effect of desilication that results in the formation of mesopores on the catalytic activity of ZSM-5 zeolite in the decomposition of N_2O was also confirmed for copper-modified samples by Zou et al. [103], who studied the catalytic activity of mesoporous Cu-ZSM-5 in nanosheet form. ZSM-5 nanosheets were synthesised using diquaternary ammonium-type surfactant $[\text{C}_{18}\text{H}_{37}\text{-N}^+(\text{CH}_3)_2\text{-C}_6\text{H}_{12}\text{-N}^+(\text{CH}_3)_2\text{-C}_6\text{H}_{13}]\text{Br}_2$ as a template and modified with copper by the ion exchange method. Cu-ZSM-5 in the form of nanosheets showed significantly higher catalytic activity in N_2O decomposition compared to conventional zeolite. The copper content in both samples was similar, as was the form of active copper species. Thus, the difference in catalytic activity was related to the modified morphology and porosity of the sample. Zeolite in the form of nanosheets was characterised by a larger surface area and volume of mesopores. Thus, the accessibility to active sites was improved. Furthermore, copper reducibility was better in the case of Cu-ZSM-5 nanosheets than in the conventional sample, which was confirmed by H_2 -TPR measurements. The authors also investigated the process of oxygen desorption from the surface of both samples using the O_2 -TPD method, and it was found that in the case of mesoporous Cu-ZSM-5 nanosheets, a faster oxygen release was observed. Additionally, during the stability test (50 h), the sample in the form of nanosheets showed much better stability than the conventional zeolitic catalysts.

Interesting catalytic results were also obtained for other zeolites with a hierarchical porous structure, e.g., with the BEA topology—Beta zeolite modified with Fe [104,105], Cu and Co [105]. In this case, mesoporous zeolites were prepared by a template-free method (under controlled conditions, with the use of hydrochloric acid) and by impregnation of the SBA-15 mesoporous material with Beta nanoseeds. The applied synthesis pathways enabled the formation of catalysts with the properties of Beta zeolite, combined with mesoporosity. In the case of the template-free method, mesopores were created between the zeolite seeds (loose packing of Beta grains), and in the case of impregnated SBA-15, parallel and uniform silica template mesopores were present in the sample, Figure 13. The improved accessibility of ion exchange positions and the improved mass transfer resulted in a high iron distribution (introduced by the post-synthesis ion exchange method, mainly in the form of isolated Fe^{3+} cations and small oligomeric Fe_xO_y species).

In contrast, modification of MCM-22 zeolite by delamination to obtain ITQ-2 with mesopores did not result in its increased catalytic activity in the decomposition of N_2O [106]. Both MCM-22 and ITQ-2 modified with iron by ion exchange with solutions of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ or $[\text{Fe}_3(\text{OCOCH}_3)_7 \cdot \text{OH} \cdot 2\text{H}_2\text{O}]\text{NO}_3$ showed high activity in N_2O decomposition. However, it seems that the delamination of MCM-22 into mesoporous ITQ-2, which is associated with a modification of zeolite properties (lower crystallinity, smaller micropore volume), ultimately results in a reduction in catalytic efficiency. Similar results were obtained in the case of MCM-22 intercalation with silica–titania pillars, resulting in MCM-36 material. Jankowska et al. [107] studied the catalytic activity of iron-exchanged MCM-22 and MCM-

36 (intercalated with silica and titania pillars) in the conversion of different nitrogen air pollutants (NO, NH₃, and N₂O). In the case of N₂O decomposition, intercalation of MCM-22 (generation of mesoporosity) did not improve its catalytic activity.

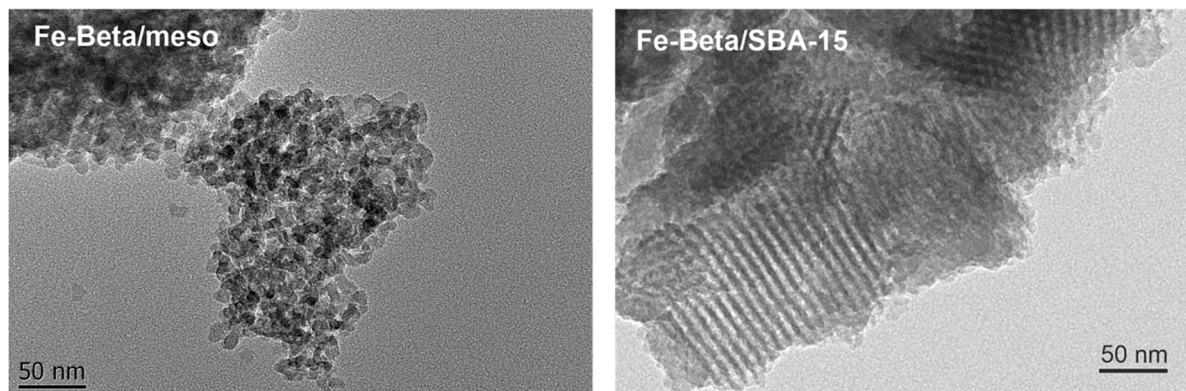


Figure 13. Morphology of mesoporous Beta zeolite, obtained by the template-free method (Fe-Beta/meso sample) and by impregnation of SBA-15 with Beta zeolite nanoseeds (Fe-Beta(A)/SBA-15 sample). Reprinted with permission from Ref. [105]. Copyright 2014 Elsevier.

In the case of N₂O decomposition, modification of zeolites (formation of the mesoporosity or hierarchical porous structure) may have a positive impact on their catalytic effectiveness. This is mainly related to the enhanced accessibility of ion exchange positions and improved internal diffusion of reactants, which influence the ion exchange process and lead to better distribution of catalytically active transition metal species, their better accessibility, and higher loading. The summary, which presents various mesoporous zeolites tested in this reaction, is presented in Table 4. It can be concluded that the studies were mainly devoted to Fe-ZSM-5 zeolite, which is connected with its high activity in the decomposition of N₂O in its conventional form. Most often, desilication at different conditions or in various combinations, e.g., with the delamination process, is applied to generate micro-mesoporous zeolitic materials. In general, the authors agree that zeolites with modified porosity are characterized by improved catalytic activity and stability due to better distribution, accessibility, reducibility, and higher loading of transition metal species. However, some exceptions to this rule have also been reported. In the case of MCM-22, zeolite modification by delamination or intercalation did not improve its catalytic activity. The modification conditions must be appropriately adjusted to obtain an optimal balance between the generated mesoporosity and partially damaged microporous zeolitic structure.

Table 4. Examples of the application of hierarchical zeolites as catalysts in N₂O decomposition.

Topology	Zeolite	Modification	Result	References
BEA	Fe-Beta	Template-free, hard-templating	Improved accessibility to ion exchange positions, and better distribution of iron species.	[105,106]
MFI	Cu-ZSM-5	Nanosheets	Higher activity, better reducibility of Cu ⁺ species. More facile desorption of oxygen. Better stability.	[103]
MFI	Fe-ZSM-5	Desilication	Higher activity, complete ion exchange, and increased accessibility to ion exchange positions.	[95–97]
MFI	Fe-ZSM-5	Desilication of Fe-sample	Higher activity, higher concentration of Fe ²⁺ , enhanced N ₂ O activation, and better O ₂ desorption.	[98]
MFI	Fe-ZSM-5	Template-free	Improved diffusion and higher iron loading. Higher activity in comparison to conventional catalysts.	[99]

Table 4. Cont.

Topology	Zeolite	Modification	Result	References
MFI	Fe-ZSM-5	Soft-templating, spherical	Improved mass transfer, and higher activity in comparison to conventional zeolite.	[100]
MFI	Fe-ZSM-5	Steaming, desilication	Higher activity, higher content of active iron species, and improved mass transport.	[101,102]
MWW	Fe-ITQ-2 Fe-MCM-36	Delamination, intercalation	Lower activity compared to conventional MCM-22 zeolite. Partially destroyed zeolitic structure (lower crystallinity, lower volume of micropores).	[106,107]

5. Other Reactions

Despite the most studied reactions related to nitrogen-containing air pollutants, such as NH_3 -SCR, NH_3 -SCO, or N_2O decomposition, other reactions related to the reduction of nitrogen air pollutants are of interest to scientists. As already discussed, NO_x reduction with ammonia is one of the main technologies used for the conversion of these pollutants into flue gases emitted by stationary sources (e.g., power stations and industrial boilers). The modified version of this method was adapted for the conversion of NO_x in diesel exhaust gases (AdBlue technology). However, NO_x can also be reduced by hydrocarbons, CO, and hydrogen (e.g., three-way catalysts). Another very promising reaction of NO conversion is its direct decomposition. This method does not require any reducing agent and leads only to nitrogen and oxygen as products; however, it is hard to find an effective catalyst that gives reasonable reaction rates. Kustova et al. [108] investigated the catalytic activity of mesoporous Cu-ZSM-5 and Cu-ZSM-11 in direct NO decomposition. The samples were prepared with the use of a hard template, carbon black particles BP-2000, and were characterised by high intracrystalline mesoporosity. In the case of both mesoporous zeolites, Cu-ZSM-5 and Cu-ZSM-11, the catalytic activity improved significantly compared to conventional zeolites, which was explained by improved accessibility to active centres and a greater contribution of dimeric and oligomeric copper species (evidenced by the NH_3 -TPD and EPR experiments). Konysheva et al. [109] studied the activity of hierarchical zeolites with BEA and MOR topology in the simultaneous reduction of N_2O and NO with propylene. BEA zeolite in the form of aggregated nanoparticles and MOR zeolite in the layered form were prepared with the use of soft templates and organic structure-directing agents and doped with indium oxide. The samples were also tested in the presence of oxygen and water vapour and showed promising activity.

In the case of N_2O , which has slight oxidative properties, it can be used as a reagent in various hydrocarbon oxidation reactions. Oxidation of benzene to phenol is an especially important reaction since phenol is an important intermediate and raw chemical in industry. The reuse of N_2O emitted from the adipic acid plant to oxidise benzene to phenol was developed by Solutia and the Boreskov Catalysis Institute and was tested in a pilot plant built by Solutia in Pensacola (Florida, USA) [110]. Fe-ZSM-5 zeolite is a very promising catalyst for this reaction, as the selectivity of phenol oxidation is almost 100% over this material, although coke formation leads to micropore blockage and fast deactivation. Thus, the application of mesoporous zeolites in this reaction seems to be very promising. Different methods have been studied for the generation of mesoporosity in Fe-ZSM-5, including desilication [110] and soft templating (resulting in different morphologies, such as layered or spherical materials) [111–114], to activate zeolitic catalysts for the oxidation of benzene with N_2O . In all cases, the improved internal mass transfer, as a result of the generated mesoporosity, improved catalytic activity and stability of Fe-ZSM-5 in this reaction, with a simultaneous reduction in the formation of carbonaceous deposits. Similar studies were performed for mesoporous zeolites used as catalysts for selective oxidation of propane with N_2O . ZSM-5 [115] and FAPO [116] zeolites modified by steaming were tested in this

reaction. It was shown that steam-activated Fe-ZSM-5 had superior activity; however, the catalyst underwent rapid deactivation by coke formation.

6. Summary

Various nitrogen-containing air pollutants such as NO, NO₂, N₂O, or NH₃ are hazardous both to human health and to the natural environment. Growing awareness of society and ever-tightening legal regulations in the field of environmental protection are driving forces for scientists to develop new techniques for emission reduction. Among the different types of catalysts used for pollutant conversion, a relatively new type of material—mesoporous zeolites modified with selected transition metals—is very promising. Zeolites, a very well-known group of materials in catalysis, can be modified by various methods (on the stage of synthesis or by post-synthesis modifications) in order to generate mesoporosity or to create a hierarchical porous structure. The idea of such modifications relates to a more open porous structure, larger surface area and volume of pores, better access to ion exchange positions, improved diffusion, and indirectly to the form, loading, and aggregation of introduced metal species, which can have a positive effect on the catalytic activity.

In this review, a brief summary of the activity of mesoporous zeolites in reactions of NO reduction with ammonia, NH₃ oxidation, and N₂O decomposition was presented. The first conclusion that can be drawn is that this scientific area is very broad and the outcomes cannot be easily generalised. The high number of zeolite types (more than 250 topologies) and high number of modification methods connected with various modification conditions or different methods of active metal introduction provide a huge number of possible pathways and results. However, in the case of considered reactions, as reported in the literature, the studies have been narrowed to a few types of zeolites and transition metals. Noticeably, scientists most frequently modified the porosity of ZSM-5 zeolite using the desilication method.

Based on the literature cited, it can be concluded that in the majority of cases, the modification of the porosity of the zeolites has a positive impact on the catalyst activity in the conversion of nitrogen pollutants. This positive impact was demonstrated by improved diffusion and accessibility to active sites, better distribution of introduced metals, enhanced redox properties, or higher loadings of metal species. However, in a few cases, hierarchically structured/mesoporous zeolites showed no improved activity or were found to be even less active than conventional zeolites. The porosity modification of zeolites led to the destruction of the starting material (lower crystallinity, weaker acidity, and ion exchange properties), including enhanced acidity of mesoporous zeolite, which can be responsible for faster deactivation of the catalyst.

In summary, the use of mesoporous zeolites as catalysts for the conversion of nitrogen pollutants has shown very promising results and should be further investigated. Careful selection of the modification method and its conditions allows for precise selection of the catalyst properties, thus increasing the final catalytic activity compared to conventional zeolite.

7. Future Perspectives and Challenges

The benefits of using mesoporous/hierarchical zeolites in the conversion of nitrogenous air pollutants are related to their clear advantage over conventional zeolites in the form of a larger and better accessible surface. Despite the direct benefits in the form of better diffusion of reagents, the modified porous structure of zeolites also affects the dispersion of active substances.

Taking into account the multitude of factors that influence the final properties of the catalyst, the main challenge is to optimise all of the synthesis parameters. Depending on the type of zeolite topology, its Si/Al ratio, synthesis or modification conditions, and finally the active metal deposition method, different final catalytic performances will be obtained. Moreover, modifications of zeolite porosity are often accompanied by a decrease in microporosity and crystallinity, so the challenge is to balance the produced mesoporosity

and the preserved zeolite properties. However, numerous studies collected in this review indicate that it is possible to increase the efficiency of conventional zeolites in the conversion of nitrogen pollutants by creating mesopores or a hierarchical porous structure. Therefore, the goal of future research will be to focus on relatively simple and inexpensive methods to enable further scaling and eventual commercialisation of this new type of catalyst. More specifically, research should be devoted to the modification of zeolite types already known for their high activity in a given reaction (e.g., CHA zeolite in the case of NH_3 -SCR) and their uncomplicated modification through a single synthesis step (such as hard-template synthesis) or easy post-synthesis modification such as steaming or desilication. It is worth noting that, from the point of view of large-scale applications, it would be beneficial to modify raw zeolites.

In summary, the commercialisation (scale-up) of systems for the catalytic elimination of nitrogen air pollutants based on mesoporous zeolites is a serious challenge that should certainly take into account the optimisation of modification procedures on a larger scale while maintaining activity and reasonable costs. This development will be the greatest challenge in this research area in the coming decades.

Author Contributions: Conceptualization, M.R. and L.C.; writing—original draft preparation, M.R.; writing—review and editing, M.R. and L.C.; supervision, L.C.; project administration, M.R. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: The original contributions presented in the study are included in the article, further inquiries can be directed to the corresponding author.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Weissenberger, T.; Machoke, A.G.F.; Reiprich, B.; Schwieger, W. Preparation and Potential Catalytic Applications of Hierarchically Structured Zeolites with Macropores. *Adv. Mater. Interfaces* **2021**, *8*, 2001653–2001672. [\[CrossRef\]](#)
2. Kerstens, D.; Smeyers, B.; Van Waeyenberg, J.; Zhang, Q.; Yu, J.; Sels, B.F. State of the Art and Perspectives of Hierarchical Zeolites: Practical Overview of Synthesis Methods and Use in Catalysis. *Adv. Mater.* **2020**, *32*, 2004690–2004737. [\[CrossRef\]](#) [\[PubMed\]](#)
3. Vu, X.H.; Armbruster, U.; Martin, A. Micro/Mesoporous Zeolitic Composites: Recent Developments in Synthesis and Catalytic Applications. *Catalysts* **2016**, *6*, 183–206. [\[CrossRef\]](#)
4. Hartmann, M.; Thommes, M.; Schwieger, M. Hierarchically-Ordered Zeolites: A Critical Assessment. *Adv. Mater. Interfaces* **2021**, *8*, 2001841–2001879. [\[CrossRef\]](#)
5. Liu, Z.; Hua, Y.; Wang, J.; Dong, X.; Tian, Q.; Han, Y. Recent progress in the direct synthesis of hierarchical zeolites: Synthetic strategies and characterization methods. *Mater. Chem. Front.* **2017**, *1*, 2195–2212. [\[CrossRef\]](#)
6. Lopez-Orozco, S.; Inayat, A.; Schwab, A.; Selvam, T.; Schwieger, W. Zeolitic materials with hierarchical porous structures. *Adv. Mater.* **2011**, *23*, 2602–2615. [\[CrossRef\]](#) [\[PubMed\]](#)
7. Wei, Y.; Parmentier, T.E.; De Jong, K.P.; Zečević, J. Tailoring and visualizing the pore architecture of hierarchical zeolites. *Chem. Soc. Rev.* **2015**, *44*, 7234–7261. [\[CrossRef\]](#) [\[PubMed\]](#)
8. Singh, B.K.; Kim, Y.; Kwon, S.; Na, K. Synthesis of Mesoporous Zeolites and Their Opportunities in Heterogeneous Catalysis. *Catalysts* **2021**, *11*, 1541. [\[CrossRef\]](#)
9. Farsana, O.P.; Kumari, P. Hierarchical Assembly of Zeolites: A Present Scenario. *Eng. Sci.* **2023**, *21*, 781.
10. Degnan, T.F. Applications of zeolites in petroleum refining. *Top. Catal.* **2000**, *13*, 349–356. [\[CrossRef\]](#)
11. Verboekend, D.; Vilé, G.; Pérez-Ramírez, J. Hierarchical Y and USY Zeolites Designed by Post-Synthetic Strategies. *Adv. Funct. Mater.* **2012**, *22*, 916–928. [\[CrossRef\]](#)
12. García-Martínez, J.; Li, K.; Krishnaiah, G. A mesostructured Y zeolite as a superior FCC catalyst—From lab to refinery. *Chem. Commun.* **2012**, *48*, 11841–11843. [\[CrossRef\]](#) [\[PubMed\]](#)
13. Li, K.; Valla, J.; García-Martínez, J. Realizing the Commercial Potential of Hierarchical Zeolites: New Opportunities in Catalytic Cracking. *ChemCatChem* **2014**, *6*, 46–66. [\[CrossRef\]](#)
14. Čejka, J.; Mintova, S. Perspectives of Micro/Mesoporous Composites in Catalysis. *Catal. Rev.* **2007**, *49*, 457–509. [\[CrossRef\]](#)
15. Ivanova, I.I.; Knyazeva, E.E. Micro-mesoporous materials obtained by zeolite recrystallization: Synthesis, characterization and catalytic applications. *Chem. Soc. Rev.* **2013**, *42*, 3671–3688. [\[CrossRef\]](#) [\[PubMed\]](#)
16. Rutkowska, M.; Chmielarz, L. Advances in synthesis of zeolitic materials with hierarchical porous structure for application in environmental catalysis. In *Advances in Materials Science Research*; NOVA Science Publisher: Hauppauge, NY, USA, 2016; Volume 22, ISBN 978-1-63483-759-0.

17. Rutkowska, M.; Macina, D.; Piwowarska, Z.; Gajewska, M.; Díaz, U.; Chmielarz, L. Hierarchically structured ZSM-5 obtained by optimized mesotemplate-free method as active catalyst for methanol to DME conversion. *Catal. Sci. Technol.* **2016**, *6*, 4849–4862. [\[CrossRef\]](#)
18. Rutkowska, M.; Macina, D.; Mirocha-Kubieñ, N.; Piwowarska, Z.; Chmielarz, L. Hierarchically structured ZSM-5 obtained by desilication as new catalyst for DME synthesis from methanol. *Appl. Catal. B Environ.* **2015**, *174*, 336–343. [\[CrossRef\]](#)
19. Wang, J.; Shi, Y.; Kong, F.; Zhou, R. Low-temperature VOCs oxidation performance of Pt/zeolites catalysts with hierarchical pore structure. *J. Environ. Sci.* **2023**, *124*, 505–512. [\[CrossRef\]](#)
20. Wang, J.; Guo, X.; Shi, Y.; Zhou, R. Synergistic effect of Pt nanoparticles and micro-mesoporous ZSM-5 in VOCs low-temperature removal. *J. Environ. Sci.* **2021**, *107*, 87–97. [\[CrossRef\]](#) [\[PubMed\]](#)
21. Holm, M.S.; Taarning, E.; Egeblad, K.; Christensen, C.H. Catalysis with hierarchical zeolites. *Catal. Today* **2011**, *168*, 3–16. [\[CrossRef\]](#)
22. Aguirre-Cruz, G.; Legorreta-Garcia, F.; Aguirre-Cruz, G.; Stanciu, L.; Aguirre-Alvarez, G. Synthesis of hierarchical silica zeolites for heterogeneous catalysis and adsorption. *Microporous Mesoporous Mater.* **2022**, *345*, 112274. [\[CrossRef\]](#)
23. Li, C.; Sun, P.; Li, F. Hierarchical zeolites-confined metal catalysts and their enhanced catalytic performances. *Chem. Asian J.* **2021**, *16*, 2795–2805. [\[CrossRef\]](#) [\[PubMed\]](#)
24. Mardiana, S.; Azhari, N.J.; Ilmi, T.; Kadja, G.T.M. Hierarchical zeolite for biomass conversion to biofuel: A review. *Fuel* **2022**, *309*, 122119. [\[CrossRef\]](#)
25. Martins, A.; Nunes, N.; Carvalho, A.P.; Martins, L.M.D.R.S. Zeolites and related materials as catalyst supports for hydrocarbon oxidation reactions. *Catalysts* **2022**, *12*, 154. [\[CrossRef\]](#)
26. Miao, C.; Wang, L.; Zhou, S.; Yu, D.; Zhang, C.; Gao, S.; Yu, X.; Zhao, Z. Preparation of Mesoporous Zeolites and Their Applications in Catalytic Elimination of Atmospheric Pollutants. *Catalysts* **2024**, *14*, 75. [\[CrossRef\]](#)
27. Verboekend, D.; Pérez-Ramírez, J. Design of hierarchical zeolite catalysts by desilication. *Catal. Sci. Technol.* **2011**, *1*, 879–890. [\[CrossRef\]](#)
28. Groen, J.C.; Moulijn, J.A.; Pérez-Ramírez, J. Desilication: On the controlled generation of mesoporosity in MFI zeolites. *J. Mater. Chem.* **2006**, *16*, 2121–2131. [\[CrossRef\]](#)
29. Silaghi, M.-C.; Chizallet, C.; Raybaud, P. Challenges on molecular aspects of dealumination and desilication of zeolites. *Microporous Mesoporous Mater.* **2014**, *191*, 82–96. [\[CrossRef\]](#)
30. Qin, Z.; Gilson, J.-P.; Valtchev, V. Mesoporous zeolites by fluoride etching. *Curr. Opin. Chem. Eng.* **2015**, *8*, 1–6. [\[CrossRef\]](#)
31. Müller, M.; Harvey, G.; Prins, R. Comparison of the dealumination of zeolites beta, mordenite, ZSM-5 and ferrierite by thermal treatment, leaching with oxalic acid and treatment with SiCl₄ by ¹H, ²⁹Si and ²⁷Al MAS NMR. *Microporous Mesoporous Mater.* **2000**, *34*, 135–147. [\[CrossRef\]](#)
32. Mumtaz, F.; Irfan, M.F.; Usman, M.R. Synthesis methods and recent advances in hierarchical zeolites: A brief review. *J. Iran. Chem. Soc.* **2021**, *18*, 2215–2229. [\[CrossRef\]](#)
33. De Oliveira Jardim, E.; Serrano, E.; Martínez, J.C.; Linares, N.; García-Martínez, J. Consecutive surfactant-templating opens up new possibilities for hierarchical zeolites. *Cryst. Growth Des.* **2020**, *20*, 515–520. [\[CrossRef\]](#)
34. Roth, W.J.; Gil, B.; Makowski, W.; Marszałek, B.; Eliášová, P. Layer like porous materials with hierarchical structure. *Chem. Soc. Rev.* **2016**, *45*, 3400–3438. [\[CrossRef\]](#) [\[PubMed\]](#)
35. Roth, W.J.; Nachtigall, P.; Morris, R.E.; Čejka, J. Two-dimensional zeolites: Current status and perspectives. *Chem. Rev.* **2014**, *114*, 4807–4837. [\[CrossRef\]](#)
36. Ramos, F.S.O.; Pietre, M.K.; Pastore, H.O. Lamellar zeolites: An oxymoron? *RSC Adv.* **2013**, *3*, 2084–2111. [\[CrossRef\]](#)
37. Hong, M.; Dong, L.; Yang, S. Organic Mesopore Generating Agents (OMeGAs) for Hierarchical Zeolites: Combining Functions on Multiple Scales. *ChemNanoMat* **2019**, *5*, 869–877. [\[CrossRef\]](#)
38. Sachse, A.; García-Martínez, J. Surfactant-Templating of Zeolites: From Design to Application. *Chem. Mater.* **2017**, *29*, 3827–3853. [\[CrossRef\]](#)
39. Egeblad, K.; Christensen, C.H.; Kustova, M.; Christensen, C.H. Templating mesoporous zeolites. *Chem. Mater.* **2008**, *20*, 946–960. [\[CrossRef\]](#)
40. Janssen, A.H.; Schmidt, I.; Jacobsen, C.J.H.; Koster, A.J.; de Jong, K.P. Exploratory study of mesopore templating with carbon during zeolite synthesis. *Microporous Mesoporous Mater.* **2003**, *65*, 59–75. [\[CrossRef\]](#)
41. Zhu, K.; Egeblad, K.; Christensen, C.H. Tailoring the porosity of hierarchical zeolites by carbon-templating. *Stud. Surf. Sci. Catal.* **2008**, *174*, 285–288.
42. Demikhova, N.R.; Rubtsova, M.I.; Kireev, G.A.; Cherednichenko, K.A.; Vinokurov, V.A.; Glotov, A.P. Micro-mesoporous catalysts based on ZSM-5 zeolite synthesized from natural clay nanotubes: Preparation and application in the isomerization of C-8 aromatic fraction. *Chem. Eng. J.* **2023**, *453*, 139581. [\[CrossRef\]](#)
43. Chen, X.; Qiu, M.; Li, S.; Yang, C.; Shi, L.; Zhou, S.; Yu, G.; Ge, L.; Yu, X.; Liu, Z.; et al. Gamma-ray irradiation to accelerate crystallization of mesoporous zeolites. *Angew. Chem. Int. Ed.* **2020**, *59*, 11325–11329. [\[CrossRef\]](#)
44. Maghfirah, A.; Ilmi, M.M.; Fajar, A.T.N.; Kadja, G.T.M. A review on the green synthesis of hierarchically porous zeolite. *Mater. Today Chem.* **2020**, *17*, 100348–100369. [\[CrossRef\]](#)
45. Shestakova, D.O.; Sashkina, K.A.; Parkhomchuk, E.V. Template-Free Synthesis of Hierarchical Zeolite ZSM-5. *Pet. Chem.* **2019**, *59*, 838–844. [\[CrossRef\]](#)

46. Wakihara, T.; Tatami, J. Top-down tuning of nanosized zeolites by bead-milling and recrystallization. *J. Jpn. Pet. Inst.* **2013**, *56*, 206–213. [\[CrossRef\]](#)
47. Tosheva, L.; Valtchev, V.P. Nanozeolites: Synthesis, crystallization mechanism, and applications. *Chem. Mater.* **2005**, *17*, 2494–2513. [\[CrossRef\]](#)
48. Fang, Y.; Hu, H. An ordered mesoporous aluminosilicate with completely crystalline zeolite wall structure. *J. Am. Chem. Soc.* **2006**, *128*, 10636–10637. [\[CrossRef\]](#) [\[PubMed\]](#)
49. Verhoef, M.J.; Kooyman, P.J.; Van der Waal, J.C.; Rigutto, M.S.; Peters, J.A.; Van Bekkum, H. Partial transformation of MCM-41 material into zeolites: Formation of nanosized MFI type crystallites. *Chem. Mater.* **2001**, *13*, 683–687. [\[CrossRef\]](#)
50. Huang, L.; Guo, W.; Deng, P.; Xue, Z.; Li, Q. Investigation of Synthesizing MCM-41/ZSM-5 Composites. *J. Phys. Chem. B* **2000**, *104*, 2817–2823. [\[CrossRef\]](#)
51. Li, S.; Li, J.; Dong, M.; Fan, S.; Zhao, T.; Wang, J.; Fan, W. Strategies to control zeolite particle morphology. *Chem. Soc. Rev.* **2019**, *48*, 885–907. [\[CrossRef\]](#)
52. Wang, K.; Dong, M.; Li, J.; Liu, P.; Zhang, K.; Wang, J.; Fan, W. Facile fabrication of ZSM-5 zeolite hollow spheres for catalytic conversion of methanol to aromatics. *Catal. Sci. Technol.* **2017**, *7*, 560–564. [\[CrossRef\]](#)
53. Wang, X.D.; Yang, W.L.; Tang, Y.; Wang, Y.J.; Fu, S.K.; Gao, Z. Fabrication of hollow zeolite spheres. *Chem. Commun.* **2000**, *21*, 2161–2162. [\[CrossRef\]](#)
54. Merilaita, N.; Vastamäki, T.; Ismailov, A.; Levänen, E.; Järveläinen, M. Stereolithography as a manufacturing method for a hierarchically porous ZSM-5 zeolite structure with adsorption capabilities. *Ceram. Int.* **2021**, *47*, 10742–10748. [\[CrossRef\]](#)
55. Magzoub, F.; Li, X.; Lawson, S.; Rezaei, F.; Rownaghi, A.A. 3D-printed HZSM-5 and 3D-HZM5@SAPO-34 structured monoliths with controlled acidity and porosity for conversion of methanol to dimethyl ether. *Fuel* **2020**, *280*, 118628–118634. [\[CrossRef\]](#)
56. Halevi, O.; Chen, T.-Y.; Lee, P.S.; Magdassi, S.; Hriljac, J.A. Nuclear wastewater decontamination by 3D-Printed hierarchical zeolite monoliths. *RSC Adv.* **2020**, *10*, 5766–5776. [\[CrossRef\]](#) [\[PubMed\]](#)
57. Chmielarz, L.; Dziembaj, R. Modified layered silicas as catalysts for conversion of nitrogen pollutants in flue gases—A review. *Catalysts* **2021**, *11*, 644. [\[CrossRef\]](#)
58. Jabłońska, M. Recent progress in the selective catalytic reduction of NO_x with NH₃ on Cu-SAPO-34 catalysts. *Mol. Catal.* **2022**, *518*, 112111. [\[CrossRef\]](#)
59. Ma, L.; Cheng, Y.; Cavataio, G.; McCabe, R.W.; Fu, L.; Li, J. Characterization of commercial Cu-SSZ-13 and Cu-SAPO-34 catalysts with hydrothermal treatment for NH₃-SCR of NO_x in diesel exhaust. *Chem. Eng. J.* **2013**, *225*, 323–330. [\[CrossRef\]](#)
60. Wang, X.; Xu, Y.; Zhao, Z.; Liao, J.; Chen, C.; Li, Q. Recent progress of metal-exchanged zeolites for selective catalytic reduction of NO_x with NH₃ in diesel exhaust. *Fuel* **2021**, *305*, 121482. [\[CrossRef\]](#)
61. Shan, Y.; Du, J.; Yu, Y.; Shan, W.; Shi, X.; He, H. Precise control of post-treatment significantly increases hydrothermal stability of in-situ synthesized Cu-zeolites for NH₃-SCR reaction. *Appl. Catal. B Environ.* **2020**, *266*, 118655. [\[CrossRef\]](#)
62. Liu, X.; Wu, X.; Weng, D.; Si, Z.; Ran, R. Evolution of copper species on Cu/SAPO-34 SCR catalysts upon hydrothermal aging. *Catal. Today* **2017**, *281*, 596–604. [\[CrossRef\]](#)
63. Paolucci, C.; Khurana, I.; Parekh, A.A.; Li, S.; Shih, A.J.; Li, H.; Albarracin-Caballero, J.D.; Yezerets, A.; Miller, J.T.; Delgass, W.N.; et al. Dynamic multinuclear sites formed by mobilized copper ions in NO_x selective catalytic reduction. *Science* **2017**, *357*, 898–903. [\[CrossRef\]](#) [\[PubMed\]](#)
64. Zhu, N.; Lian, Z.; Zhang, Y.; Shan, W.; He, H. The promotional effect of H₂ reduction treatment on the low-temperature NH₃-SCR activity of Cu/SAPO-18. *Appl. Surf. Sci.* **2019**, *483*, 536–544. [\[CrossRef\]](#)
65. Xia, Y.; Zhan, W.; Guo, Y.; Guo, Y.; Lu, G. Fe-Beta zeolite for selective catalytic reduction of NO_x with NH₃: Influence of Fe content. *Chin. J. Catal.* **2016**, *37*, 2069–2078. [\[CrossRef\]](#)
66. Oord, R.; ten Have, I.C.; Arends, J.M.; Hendriks, F.C.; Schmidt, J.; Lezcano-Gonzalez, I.; Weckhuysen, B.M. Enhanced activity of desilicated Cu-SSZ-13 for the selective catalytic reduction of NO_x and its comparison with steamed Cu-SSZ-13. *Catal. Sci. Technol.* **2017**, *7*, 3851–3862. [\[CrossRef\]](#)
67. Rutkowska, M.; Pacia, I.; Basag, S.; Kowalczyk, A.; Piwowarska, Z.; Duda, M.; Tarach, K.A.; Góra-Marek, K.; Michalik, M.; Díaz, U.; et al. Catalytic performance of commercial Cu-ZSM-5 zeolite modified by desilication in NH₃-SCR and NH₃-SCO processes. *Microporous Mesoporous Mater.* **2017**, *246*, 193–206. [\[CrossRef\]](#)
68. Pérez-Ramírez, J.; Verboekend, D.; Bonilla, A.; Abelló, S. Zeolite catalysts with tunable hierarchy factor by pore-growth moderators. *Adv. Funct. Mater.* **2009**, *19*, 3972–3979. [\[CrossRef\]](#)
69. Ma, J.; Weng, D.; Wu, X.; Si, Z.; Wu, Z. Highly dispersed iron species created on alkali-treated zeolite for ammonia SCR. *Prog. Nat. Sci.* **2013**, *23*, 493–500. [\[CrossRef\]](#)
70. Zhang, T.; Qiu, F.; Li, J. Design and synthesis of core-shell structured meso-Cu-SSZ-13@mesoporous aluminosilicate catalyst for SCR of NO_x with NH₃: Enhancement of activity, hydrothermal stability and propene poisoning resistance. *Appl. Catal. B Environ.* **2016**, *195*, 48–58. [\[CrossRef\]](#)
71. Liu, J.; Yu, F.; Liu, J.; Cui, L.; Zhao, Z.; Li, Y.; Wei, Y.; Sun, Q. Synthesis and kinetics investigation of meso-microporous Cu-SAPO-34 catalysts for the selective catalytic reduction of NO with ammonia. *J. Environ. Sci.* **2016**, *48*, 45–58. [\[CrossRef\]](#)
72. Peng, C.; Yan, R.; Peng, H.; Mi, Y.; Liang, J.; Liu, W.; Wang, X.; Song, G.; Wu, P.; Liu, F. One-pot synthesis of layered mesoporous ZSM-5 plus Cu ion-exchange: Enhanced NH₃-SCR performance on Cu-ZSM-5 with hierarchical pore structures. *J. Hazard. Mater.* **2020**, *385*, 121593. [\[CrossRef\]](#) [\[PubMed\]](#)

73. Wang, P.; Li, Z.; Wang, X.; Tong, Y.; Yuan, F.; Zhu, Y. One-pot synthesis of Cu/SAPO-34 with hierarchical pore using cupric citrate as a copper source for excellent NH_3 -SCR of NO performance. *ChemCatChem* **2020**, *12*, 4871–4878. [\[CrossRef\]](#)
74. Li, R.; Wang, P.; Ma, S.; Yuan, F.; Li, Z.; Zhu, Y. Excellent selective catalytic reduction of NO_x by NH_3 over Cu/SAPO-34 with hierarchical pore structure. *Chem. Eng. J.* **2020**, *379*, 122376. [\[CrossRef\]](#)
75. Liang, J.; Tao, J.; Mi, Y.; Liu, W.; Wang, Z.; Li, Z.; Wu, D.; Wu, P.; Peng, H. Unraveling the boosting low-temperature performance of ordered mesoporous Cu-SSZ-13 catalyst for NO_x reduction. *Chem. Eng. J.* **2021**, *409*, 128238. [\[CrossRef\]](#)
76. Świąs, A.; Kowalczyk, A.; Rutkowska, M.; Díaz, U.; Palomares, A.E.; Chmielarz, L. Ferrierite and Its Delaminated and Silica-Intercalated Forms Modified with Copper as Effective Catalysts for NH_3 -SCR Process. *Catalysts* **2020**, *10*, 734. [\[CrossRef\]](#)
77. Rutkowska, M.; Díaz, U.; Palomares, A.E.; Chmielarz, L. Cu and Fe modified derivatives of 2D MWW-type zeolites (MCM-22, ITQ-2 and MCM-36) as new catalysts for DeNO_x process. *Appl. Catal. B Environ.* **2015**, *168*, 531–539. [\[CrossRef\]](#)
78. Yue, Y.; Liu, B.; Lv, N.; Wang, T.; Bi, X.; Zhu, H.; Yuan, P.; Bai, Z.; Cui, Q.; Bao, X. Direct synthesis of hierarchical FeCu-ZSM-5 zeolite with wide temperature window in selective catalytic reduction of NO by NH_3 . *ChemCatChem* **2019**, *11*, 4744–4754. [\[CrossRef\]](#)
79. Jabłońska, M.; Robles, A.M. A Comparative Mini-Review on Transition Metal Oxides Applied for the Selective Catalytic Ammonia Oxidation (NH_3 -SCO). *Materials* **2022**, *15*, 4770. [\[CrossRef\]](#) [\[PubMed\]](#)
80. Chmielarz, L.; Jabłońska, M. Advances in selective catalytic oxidation of ammonia to dinitrogen: A review. *RSC Adv.* **2015**, *5*, 43408–43431. [\[CrossRef\]](#)
81. Lan, T.; Zhao, Y.; Deng, J.; Zhang, J.; Shi, L.; Zhang, D. Selective catalytic oxidation of NH_3 over noble metal-based catalysts: State of the art and future prospects. *Catal. Sci. Technol.* **2020**, *10*, 5792–5810. [\[CrossRef\]](#)
82. Jabłońska, M. Progress on Selective Catalytic Ammonia Oxidation (NH_3 -SCO) over Cu Containing Zeolite-Based Catalysts. *ChemCatChem* **2020**, *12*, 4490–4500. [\[CrossRef\]](#)
83. Góra-Marek, K.; Tarach, K.; Piwowarska, Z.; Łaniecki, M.; Chmielarz, L. Ag-loaded zeolites Y and USY as the catalysts for selective ammonia oxidation. *Catal. Sci. Technol.* **2016**, *6*, 1651–1660. [\[CrossRef\]](#)
84. Góra-Marek, K.; Brylewska, K.; Tarach, K.; Rutkowska, M.; Jabłońska, M.; Choi, M.; Chmielarz, L. IR studies of Fe modified ZSM-5 zeolites of diverse mesopore topologies in the terms of their catalytic performance in NH_3 -SCR and NH_3 -SCO processes. *Appl. Catal. B Environ.* **2015**, *179*, 589–598. [\[CrossRef\]](#)
85. Borcuch, A.; Rutkowska, M.; Marzec, A.; Kowalczyk, A.; Michalik, M.; Moreno, J.M.; Díaz, U.; Chmielarz, L. Selective ammonia oxidation over ZSM-5 zeolite: Impact of catalyst's support porosity and type of deposited iron species. *Catal. Today* **2020**, *348*, 223–229. [\[CrossRef\]](#)
86. Rutkowska, M.; Duda, M.; Macina, D.; Górecka, S.; Dębek, R.; Moreno, J.M.; Díaz, U.; Chmielarz, L. Mesoporous Beta zeolite functionalisation with Fe_xCr_y oligocations; catalytic activity in the NH_3 -SCO process. *Microporous Mesoporous Mater.* **2019**, *278*, 1–13. [\[CrossRef\]](#)
87. Świąs, A.; Rutkowska, M.; Kowalczyk, A.; Díaz, U.; Palomares, A.E.; Chmielarz, L. Ferrierite and its delaminated forms modified with copper as effective catalysts for NH_3 -SCO process. *Materials* **2020**, *13*, 4885. [\[CrossRef\]](#)
88. Wang, Z.; Sun, Q.; Wang, D.; Hong, Z.; Qu, C.; Li, X. Hollow ZSM-5 zeolite encapsulated Ag nanoparticles for SO_2 -resistant selective catalytic oxidation of ammonia to nitrogen. *Sep. Purif. Technol.* **2019**, *209*, 1016–1026. [\[CrossRef\]](#)
89. Kapteijn, F.; Rodriguez-Mirasol, J.; Moulijn, J.A. Heterogeneous catalytic decomposition of nitrous oxide. *Appl. Catal. B Environ.* **1996**, *9*, 25–64. [\[CrossRef\]](#)
90. Liu, Z.; He, F.; Ma, L.; Peng, S. Recent advances in catalytic decomposition of N_2O on noble metal and metal oxide catalysts. *Catal. Surv. Asia* **2016**, *20*, 121–132. [\[CrossRef\]](#)
91. Zhang, T.; Qiu, Y.; Liu, G.; Chen, J.; Peng, Y.; Liu, B.; Li, J. Nature of active Fe species and reaction mechanism over high-efficiency Fe/CHA catalysts in catalytic decomposition of N_2O . *J. Catal.* **2020**, *392*, 322–335. [\[CrossRef\]](#)
92. Cao, H.; Yuan, X.; Du, J.; Ren, M.; Wang, Y.; Wang, X.; Shan, Y.; He, H. High-temperature treatment promotes N_2O decomposition over Fe-impregnated Al-rich SSZ-13 zeolites. *Catal. Today* **2024**, *433*, 114670. [\[CrossRef\]](#)
93. Zhang, R.; Liu, N.; Lei, Z.; Chen, B. Selective transformation of various nitrogen-containing exhaust gases toward N_2 over zeolite catalysts. *Chem. Rev.* **2016**, *116*, 3658–3721. [\[CrossRef\]](#)
94. Zhang, X.; Shen, Q.; He, C.; Ma, C.; Cheng, J.; Liu, Z.; Hao, Z. Decomposition of nitrous oxide over Co-zeolite catalysts: Role of zeolite structure and active site. *Catal. Sci. Technol.* **2012**, *2*, 1249–1258. [\[CrossRef\]](#)
95. Melián-Cabrera, I.; Espinosa, S.; Groen, J.C.; v/d Linden, B.; Kapteijn, F.; Moulijn, J.A. Utilizing full-exchange capacity of zeolites by alkaline leaching: Preparation of Fe-ZSM5 and application in N_2O decomposition. *J. Catal.* **2006**, *238*, 250–259. [\[CrossRef\]](#)
96. Wu, M.; Chen, X.; Zhong, L.; Wang, H.; Zhang, X.; Shen, Q.; Wei, W.; Sun, Y. Comparison of alkaline pre-treatment of MFI zeolites for N_2O decomposition: Different zeolite sources. *Greenh. Gases Sci. Technol.* **2016**, *6*, 710–723. [\[CrossRef\]](#)
97. Shen, Q.; Zhang, L.; Wu, M.; He, C.; Wei, W.; Sun, N.; Sun, Y. Postsynthesis of mesoporous ZSM-5 zeolites with TPAOH-assisted desilication and determination of activity performance in N_2O decomposition. *J. Porous Mater.* **2017**, *24*, 759–767. [\[CrossRef\]](#)
98. Groen, J.C.; Brückner, A.; Berrier, E.; Maldonado, L.; Moulijn, J.A.; Pérez-Ramírez, J. Iron site modification upon alkaline treatment of Fe-ZSM-5 zeolites—Opportunities for improved N_2O decomposition activity. *J. Catal.* **2006**, *243*, 212–216. [\[CrossRef\]](#)
99. Shen, Q.; Zhang, L.; Wu, M.; Wang, H.; Sun, N.; Wei, W.; Sun, Y. High-silica nanoflower hierarchical Fe-MFI with excellent catalytic performance for N_2O decomposition. *Mater. Res. Bull.* **2017**, *87*, 1–5. [\[CrossRef\]](#)

100. Liu, G.; Zhuang, J.; Yang, F.; Xiao, Q.; Zhong, Y.; Zhu, W. N₂O direct decomposition over hierarchical FeZSM-5 catalysts. *Adv. Mater. Res.* **2012**, *518–523*, 2593–2596. [\[CrossRef\]](#)
101. Pérez-Ramírez, J.; Kapteijn, F.; Groen, J.C.; Doménech, A.; Mul, G.; Moulijn, J.A. Steam-activated FeMFI zeolites. Evolution of iron species and activity in direct N₂O decomposition. *J. Catal.* **2003**, *214*, 33–45. [\[CrossRef\]](#)
102. Pérez-Ramírez, J. Active iron sites associated with the reaction mechanism of N₂O conversions over steam-activated FeMFI zeolites. *J. Catal.* **2004**, *227*, 512–522. [\[CrossRef\]](#)
103. Zou, W.; Xie, P.; Hua, W.; Wang, Y.; Kong, D.; Yue, Y.; Ma, Z.; Yang, W.; Gao, Z. Catalytic decomposition of N₂O over Cu-ZSM-5 nanosheets. *J. Mol. Catal. A Chem.* **2014**, *394*, 83–88. [\[CrossRef\]](#)
104. Rutkowska, M.; Chmielarz, L.; Macina, D.; Piwowarska, Z.; Dudek, B.; Adamski, A.; Witkowski, S.; Sojka, Z.; Obalová, L.; Van Oers, C.J.; et al. Catalytic decomposition and reduction of N₂O over micro-mesoporous materials containing Beta zeolite nanoparticles. *Appl. Catal. B Environ.* **2014**, *146*, 112–122. [\[CrossRef\]](#)
105. Rutkowska, M.; Piwowarska, Z.; Micek, E.; Chmielarz, L. Hierarchical Fe-, Cu- and Co-Beta zeolites obtained by mesotemplate-free method. Part I: Synthesis and catalytic activity in N₂O decomposition. *Microporous Mesoporous Mater.* **2015**, *209*, 54–65. [\[CrossRef\]](#)
106. Rutkowska, M.; Jankowska, A.; Różycka-Dudek, E.; Dubiel, W.; Kowalczyk, A.; Piwowarska, Z.; Llopis, S.; Díaz, U.; Chmielarz, L. Modification of MCM-22 Zeolite and Its Derivatives with Iron for the Application in N₂O Decomposition. *Catalysts* **2020**, *10*, 1139. [\[CrossRef\]](#)
107. Jankowska, A.; Kowalczyk, A.; Rutkowska, M.; Mozgawa, W.; Gil, B.; Chmielarz, L. Silica and silica–titania intercalated MCM-36 modified with iron as catalysts for selective reduction of nitrogen oxides—The role of associated reactions. *Catal. Sci. Technol.* **2020**, *10*, 7940–7954. [\[CrossRef\]](#)
108. Kustova, M.Y.; Rasmussen, S.B.; Kustov, A.L.; Christensen, C.H. Direct NO decomposition over conventional and mesoporous Cu-ZSM-5 and Cu-ZSM-11 catalysts: Improved performance with hierarchical zeolites. *Appl. Catal. B Environ.* **2006**, *67*, 60–67. [\[CrossRef\]](#)
109. Konyshcheva, K.M.; Boichuk, T.M.; Shvets, O.V. Effect of structural, size, and acid characteristics of hierarchical BEA and MOR zeolites on their activity in the catalytic reduction of N₂O and NO by propylene. *Theor. Exp. Chem.* **2016**, *52*, 90–96. [\[CrossRef\]](#)
110. Pérez-Ramírez, J.; Kapteijn, F.; Schöffel, K.; Moulijn, J.A. Formation and control of N₂O in nitric acid production: Where do we stand today? *Appl. Catal. B Environ.* **2003**, *44*, 117–151. [\[CrossRef\]](#)
111. Zhang, F.; Chen, X.; Zhuang, J.; Xiao, Q.; Zhong, Y.; Zhu, W. Direct oxidation of benzene to phenol by N₂O over meso-Fe-ZSM-5 catalysts obtained via alkaline post-treatment. *Catal. Sci. Technol.* **2011**, *1*, 1250–1255. [\[CrossRef\]](#)
112. Li, L.; Meng, Q.; Wen, J.; Wang, J.; Tu, G.; Xu, C.; Zhang, F.; Zhong, Y.; Zhu, W.; Xiao, Q. Improved performance of hierarchical Fe-ZSM-5 in the direct oxidation of benzene to phenol by N₂O. *Microporous Mesoporous Mater.* **2016**, *227*, 252–257. [\[CrossRef\]](#)
113. Koekkoek, A.J.J.; Kim, W.; Degirmenci, V.; Xin, H.; Ryoo, R.; Hensen, E.J.M. Catalytic performance of sheet-like Fe/ZSM-5 zeolites for the selective oxidation of benzene with nitrous oxide. *J. Catal.* **2013**, *299*, 81–89. [\[CrossRef\]](#)
114. Xin, H.; Koekkoek, A.; Yang, Q.; van Santen, R.; Li, C.; Hensen, E.J.M. A hierarchical Fe/ZSM-5 zeolite with superior catalytic performance for benzene hydroxylation to phenol. *Chem. Commun.* **2009**, 7590–7592. [\[CrossRef\]](#) [\[PubMed\]](#)
115. Pérez-Ramírez, J.; Kondratenko, E.V. Steam-activated FeMFI zeolites as highly efficient catalysts for propane and N₂O valorisation via oxidative conversions. *Chem. Commun.* **2003**, 2152–2153. [\[CrossRef\]](#)
116. Wei, W.; Moulijn, J.A.; Mul, G. FAPO and Fe-TUD-1: Promising catalysts for N₂O mediated selective oxidation of propane? *J. Catal.* **2009**, *262*, 1–8. [\[CrossRef\]](#)

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.